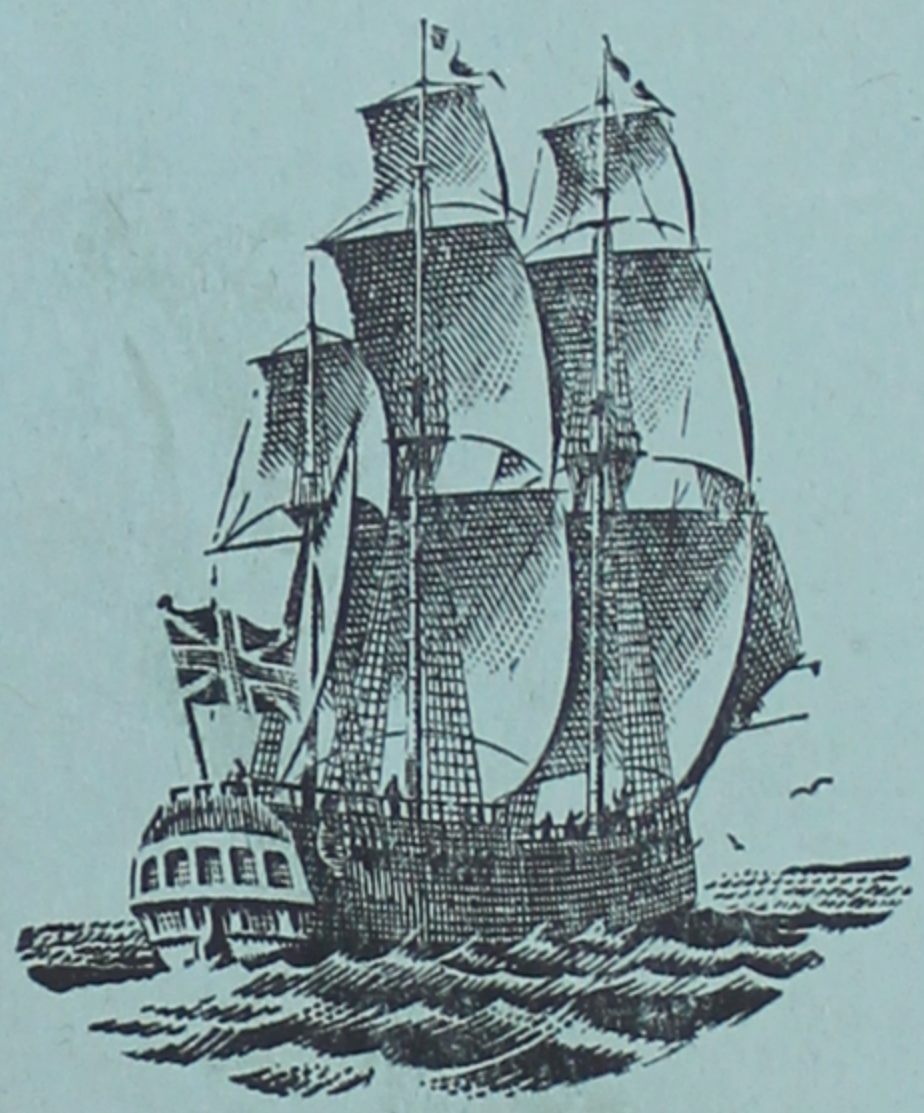
14/4

ENDEAVOUR



Volume VI Number 21

JANUARY 1947

The drawing on the cover is of the barque Endeavour, *which, commanded by Captain James Cook and carrying a number of scientific workers, was sent out by the British Admiralty in* 1768 *to chart the South Pacific Ocean and observe the transit of Venus*

Science
580
H74 &E

CONTENTS

Editorial:
The Centenary of Anaesthesia 1

The Influence of Man on Marine Life 3
C. M. YONGE, D.Sc., F.R.S.

Sydney Young, 1857–1937 11
J. TIMMERMANS, D.Sc.

Some Applications of Optical Crystallography 15
N. H. HARTSHORNE, M.C., M.Sc., Ph.D., F.R.I.C.

The Principles of Chromatography 21
A. J. P. MARTIN, M.A., Ph.D.

The Chemical Society of London 28

Organosilicon Compounds and their Industrial Development 29
D. V. N. HARDY, B.Sc., Ph.D., A.R.I.C.

The Senses of Bats 36
BRIAN VESEY-FITZGERALD, F.L.S., F.R.E.S., M.B.O.U.

The Meaning of Resonance in Quantum Chemistry 42
C. A. COULSON, M.A., D.Sc., F.R.S.E.

Book Reviews 47

Notes on Contributors *cover iii*

Cost

PRICE FIVE SHILLINGS

ENDEAVOUR

A quarterly review designed to record the progress of the sciences in the service of mankind

19780
18.3.61
SRINAGAR

VOLUME VI JANUARY 1947 NUMBER 21

The centenary of anaesthesia

It is impossible to assign the discovery of anaesthesia to any one person or to any one date, but so many events of fundamental importance in the history of anaesthetics occurred about a hundred years ago that the centenary of anaesthesia may rightly be commemorated at this time. In this connection it is appropriate to remember that, although anaesthetics are used almost exclusively by the medical and dental professions, their discovery and development owe much to the work of the pure scientist. The entire history of anaesthesia is, in fact, an illustration of the fruitful results of close collaboration between physicians and scientists.

Two outstandingly important dates in the history of anaesthesia are 16th October, 1846, when William Thomas Green Morton successfully demonstrated anaesthesia with ether before a gathering of surgeons at Boston, Massachusetts, and 4th November, 1847, when James Young Simpson and Drs Keith and Matthews Duncan recovered their senses underneath Simpson's dining-room table after testing chloroform, a drug 'far better and stronger than ether.' Chloroform and ether remained pre-eminent in surgical anaesthesia for decades, and both, despite the development and acceptance of many others, are still widely employed. These two events represented the culmination of earlier research by workers who, though they failed to achieve the goal of establishing anaesthesia in general medical practice, went far along the road towards it.

The first discovery of direct preliminary importance was the isolation of oxygen by Priestley in 1774. The physiological significance of the new gas was quickly appreciated by Lavoisier, who in the period 1774–85 elucidated the composition of the atmosphere and established the main principles of the respiratory process. These discoveries led to the development of pneumatic medicine, which concerned itself with the treatment of disease by the inhalation of gases. A noteworthy pioneer in pneumatic medicine was Thomas Beddoes, a lecturer in chemistry at Oxford. In 1794 he established the Pneumatic Institution at Clifton, Bristol, in order to pursue his investigations. One of the substances Beddoes studied was 'sulphuric ether,' the vapour of which he found to be of value in treating pains in the chest. Among those whom Beddoes attracted to Bristol was the young Humphry Davy. When Davy became superintendent of the Pneumatic Institute he was scarcely twenty years of age, but his enthusiasm for chemistry outweighed his youthful inexperience. One of his first tasks was to investigate the chemical and physiological properties of nitrous oxide, and in April 1799 he discovered that this gas was not only respirable but that, when respired, it produced a state of intoxication in which pain was deadened. He recognized the potential value of the gas in surgery, for in 1800 he wrote: 'nitrous oxide . . . appears capable of destroying physical pain, (and) it may probably be used with advantage during surgical operations in which no great effusion of blood takes place.' Unfortunately Davy himself made little effort to press this claim, so that the medical profession did not investigate it until many years later. Davy had, however, noticed another quality of nitrous oxide, namely its power of inducing a curious hilarity, which earned for it the name of 'laughing gas.' So pleasurable was the sensation that laughing-gas parties became popular in the early nineteenth century. It was owing to this frivolous application that the gas remained familiar and, nearly fifty years after Davy's original observations, eventually found its rightful place among surgical anaesthetics. In 1818 it was suggested, possibly by Michael Faraday, that ether vapour would produce the same kind of hilarity

as nitrous oxide, and very soon ether too was inhaled at fashionable parties.

At about this time a British physician named Henry Hill Hickman, who practised in Shropshire, found that surgical operations could be painlessly performed on animals after causing them to inhale carbon dioxide. He published his results in 1824, but in the absence of any support from professional colleagues did not attempt to apply his method to human beings.

Meanwhile the fashion of laughing gas and ether frolics had spread to the United States. In the course of one of them C. W. Long, a physician of Georgia, observed that while under the influence of ether his guests often bruised themselves quite severely without feeling pain. In the period 1842–4 he successfully used ether anaesthesia for several minor surgical operations. In December 1844 a Connecticut dentist, Horace Wells, attended a nitrous oxide party and made the same observation as Long had done at the ether party. Next day he induced a colleague to extract one of his teeth for him after he had inhaled nitrous oxide. Wells felt no pain, and thenceforth used nitrous oxide anaesthesia in his dental practice. Unfortunately, when Wells and his fellow dentist Morton gave a public demonstration in Boston it was a failure, and his method was discredited. Morton was not discouraged, however, and determined to try ether vapour in place of nitrous oxide. On the advice of a chemical friend, C. T. Jackson, Morton procured a very pure sample of ether and used this successfully during the extraction of a tooth. On 16th October, 1846, Morton gave his now famous demonstration of the use of ether anaesthesia in surgery before a medical and scientific audience at Boston. This demonstration was a complete success. The sceptics were convinced, and the principle of ether anaesthesia was quickly accepted by the medical profession in the United States, in England, in France, and then throughout the world.

Thirteen months later James Young Simpson, seeking a more tractable substance than ether, successfully demonstrated in Edinburgh the valuable anaesthetic qualities of chloroform. Although this agent was soon found to be more dangerous than ether, the more precise control with which it could be administered soon made it the more popular of the two.

For many years the development of anaesthesia was confined to the perfection of techniques for administering chloroform, ether, and nitrous oxide. In 1884, however, a great step forward was made when Carl Koller introduced cocaine into ophthalmic surgery and this laid the foundation of the modern technique of local anaesthesia. In doing so he was in a sense reverting to a very old method, for such drugs as opium and mandragora were well known to the ancients as analgesics, and formed part of the normal equipment of physicians. Their use was, however, hazardous, owing to the absence of methods of standardization. Koller revived interest in substances of this kind at a time when medical and scientific knowledge was sufficiently developed to permit their use with comparative safety.

Chemists in particular quickly recognized the opportunities presented by the need for new and better anaesthetics. From investigation of the structures of natural substances such as cocaine and morphine they quickly turned to the synthesis of drugs unknown in nature, modelling them first on the natural products and later investigating totally new classes of compounds. In consequence the physician's choice of anaesthetics multiplied itself with almost bewildering rapidity. Ether, chloroform, and nitrous oxide remain in general use, but to them now must be added such substances as ethyl chloride, vinyl ether (vinesthene), trichlorethylene (trilene), cyclopropane, pentothal, kemithan, procaine, and nupercaine.

The use of anaesthetics in surgery was rightly described by Sir William Osler as the greatest single discovery in the history of medicine, and the contribution it has made, and is yet to make, to the relief of human suffering is immeasurable. At a time when the destructiveness of applied science tends to obscure its far greater services to human welfare, scientists may well pride themselves on their share both in the discovery and in the effective development of surgical anaesthesia.

Editor: E. J. HOLMYARD, M.A., M.Sc., D.Litt., F.R.I.C.
Deputy Editor: TREVOR I. WILLIAMS, B.A., B.Sc., D.Phil.
Foreign Editor: J. A. WILCKEN, B.Sc., Ph.D.

Imperial Chemical Industries, Nobel House, Buckingham Gate, London, S.W.1.

The influence of man on marine life

C. M. YONGE

Man's direct influence on marine life is of comparatively recent origin, for until about two hundred years ago the amount of fishing and whaling that was carried on was too small to upset the equilibrium of nature. With improved ships, apparatus, and technique, however, came a vast and indiscriminate slaughter of marine life, and some species were exterminated altogether. There is now a general realization that wise cultivation of the sea is as necessary as wise cultivation of the land. Professor Yonge gives a broad survey of the problem.

Man has had a profound effect on terrestrial life. Hunting, first with flint tools and eventually with precise weapons, led to the extinction, for instance, of the bear, wolf, and boar in Britain and to the almost complete extinction of the bison of North America. Like the big game of Africa, this animal has been saved only by tardy methods of conservation. Fur-bearing animals have been remorselessly trapped. The faunae of the earth have been irreparably impoverished by the senseless destruction of unique birds such as the dodo and the great auk. Cultivation of crops and domestication of animals modified plants and animals so greatly that the exact origin of some is now obscure, and also effected far-reaching changes in the balance of nature. The greater the crops, the more the pests—insects, rodents, and birds especially—that were attracted.

With the full discovery of the world by western man, his crops and domestic animals were introduced into the new lands of America, Africa, and Australasia, and many of the foreign plants were brought back—accompanied all too frequently by foreign pests. Often for sentimental reasons, hosts of other plants and animals were similarly transported. This indiscriminate mixing of fauna and of flora led to disasters such as the plague of rabbits and of prickly pear in Australia, and that of bramble thickets spread by the introduction of the starling into New Zealand. Man, in despair, turned to nature to redress the balance he had wantonly destroyed, and, after some failures, there were developed methods of biological control which today are clearing the prickly pear from Australia and destroying the aphid pests of Californian orchards. But, despite the rigorous care enforced by bitter experience, the spread of life continues. The chance introduction of a malaria-carrying mosquito, *Anopheles gambiae*, from West Africa into Brazil in 1930 caused a terrible epidemic, overcome only after heroic measures by the Rockefeller Foundation.

Life in the sea has been much less affected by man. In the obscurity of its depths and in the breadth of its oceans animals are difficult to hunt to extinction, while most of the marine vegetation and the bulk of the diverse invertebrate fauna are useless to man. In the sea, it has been said, man reaps without sowing, and this is largely true. It follows that in this case the responsibility of ownership which came with the domestication of animals and the care of crops has rarely displaced the unconsidered greed of the hunter. This is nowhere better shown than in man's pursuit of the marine mammals.

There are three groups of these: the sirenia or sea cows, the marine carnivora such as seals and walruses, and the cetacea comprising the whales, dolphins, and porpoises. The sirenia are a small group of obscure origin and grotesque form. They inhabit inshore and estuarine waters, feeding on marine vegetation. They consisted, until recently, of three groups, the Indo-Pacific dugong, the manatee of the tropical Atlantic, and the much larger northern sea cow of the North Pacific. The first two survive, although actively hunted—fortunately mainly by native tribes—for their flesh and blubber. The sea cow became extinct some thirty years after its discovery in 1741 by the young German naturalist Georg Steller, who accompanied Behring's pioneer voyage to the North Pacific. Under the greatest difficulties, while marooned with unwilling helpers on Behring Island, he dissected and described the animal. The Russian hunters and traders who followed Behring quickly exterminated it, and, apart from Steller's description, there remain for study only a few skeletons. The destruction of the sea cow is the greatest blow yet dealt by man to the marine fauna, equivalent to that of the equally remarkable, harmless, and locally distributed dodo.

The walrus once occurred in vast numbers throughout the north Pacific and the Atlantic, where it extended as far south as Nova Scotia and

occasionally reached the shores of Britain. Following wholesale slaughter, such as that of 900 in one day near Spitsbergen in 1852 and that indicated by an annual import of 12,000 tusks into San Francisco alone between 1870 and 1880, it has become restricted to far northern waters. Many seals have suffered similar destruction, in particular those that breed in rookeries, like the Atlantic grey seal, and also the Greenland seal, which is the most important animal in the Newfoundland seal fishery, and the immense elephant seals (figure 1). Of these, the Californian species is now rare, but the naturalists of the *Discovery* Expedition found that the Antarctic species, which had been hunted on such a scale that it was reported virtually extinct a century ago, has reached a population of some 100,000 around South Georgia, where hunting is now annually confined to definite regions of the coast. A warm-water seal, once widely hunted in the West Indies, is now extremely rare.

These animals are sought for their blubber and flesh, but the eared seals, or sea lions, include the fur seals as much prized for their pelts as are sable, beaver, or silver fox on land. Formerly, various species abounded in northern and southern waters, but in the latter they have been almost exterminated, although there is some hope that they may be re-established in South Georgia. The greatest fishery of all was on the Pribilov Islands in the Behring Sea, some three hundred miles from Alaska. These islands were discovered by the Russians in 1786. There the vast rookery, with each huge bull gathering a harem sometimes exceeding one hundred females, and continuously fighting intruding males, must have presented an amazing spectacle. At the hands of Russian and American sealers upwards of two million seals were killed in fifty years. When the United States acquired the islands in 1867, attempts to control pelagic (open water) sealing in the Behring Sea led to international complications, and so to arbitration by a tribunal in Paris. This was followed by two Anglo-American commissions sent to the Pribilov Islands in 1891 and 1896–7. Eventually, pelagic sealing was prohibited by international agreement, and killing on the islands was restricted to the needs for food of the local population. Gradually the seal population recovered, and by confining hunting to the males, one bull to forty bearing cows being adequate for breeding, a rational control has been achieved.

It was the Russians also who discovered the delightful sea otter on the coast of Siberia. This rarest and most valuable of fur-bearing animals was hunted ruthlessly from there across the Aleutian Islands and south to California, where British and American hunters were at work. Almost complete extinction was again followed by international protection early in this century. Subsequent recovery has been slow, but populations of some two thousand in northern regions, and two hundred in southern, were estimated in 1939.

Helpless exposure on or near land invited slaughter of sea cows, seals, and sea otters. A similar fate has befallen the cetaceans, which include the largest animals ever to be evolved—the blue and fin whales—and which are so superbly adapted for aquatic life that they are even born in the sea. The tragic story of their ruthless hunting by man, which was begun by the Basques in the tenth century and has culminated in mass destruction by whale chasers operating from great factory ships in the Antarctic, has recently been related in ENDEAVOUR[1] and need not be retold.

Man the hunter has thus inflicted terrible loss on the marine mammals; fortunately it has not been worth his while, except in the one instance of the sea cow, to hunt them to final extinction. He has also, with the elaboration of increasingly efficient instruments of capture, made grave inroads into the stock of many of the more important food fishes. Here attention must be confined to the history of the European fishing grounds, in the exploitation of which Britain has played a leading part. The growth of the modern trawling industry dates from that of big industrial towns and the establishment of rapid transport between them and the fishing ports. The first North Sea trawlers came from Brixham in Devon. Originally in open boats, and later in two-masted smacks, the fishermen gradually extended their activities as far as the rich Dogger Bank. Towards the end of the last century steam trawlers employing the highly efficient otter trawl began to replace the sailing vessels, and to range as far north as the Barents Sea and as far south as Morocco. This wider range was necessary because the fish became increasingly fewer and smaller on the original grounds. Evidence of overfishing was given before a series of royal commissions but no action was taken, the extension of fishing to new areas tending to obscure the effects of depletion. Then came the war of 1914–18, which imposed a close season on fishing. The result after the war was striking: fish had

[1] L. Harrison Matthews, ENDEAVOUR, July 1946, p. 116.



FIGURE 1 – *A herd of elephant seals on a beach in South Georgia. The figure of the sealer shows the size of the bull.*
(Reproduced by courtesy of Dr L. Harrison Matthews.)



FIGURE 2 – *Japanese oysters* (Ostrea gigas) *in Ladysmith Bay, Vancouver Island, where they flourish after transplantation from Japan.*

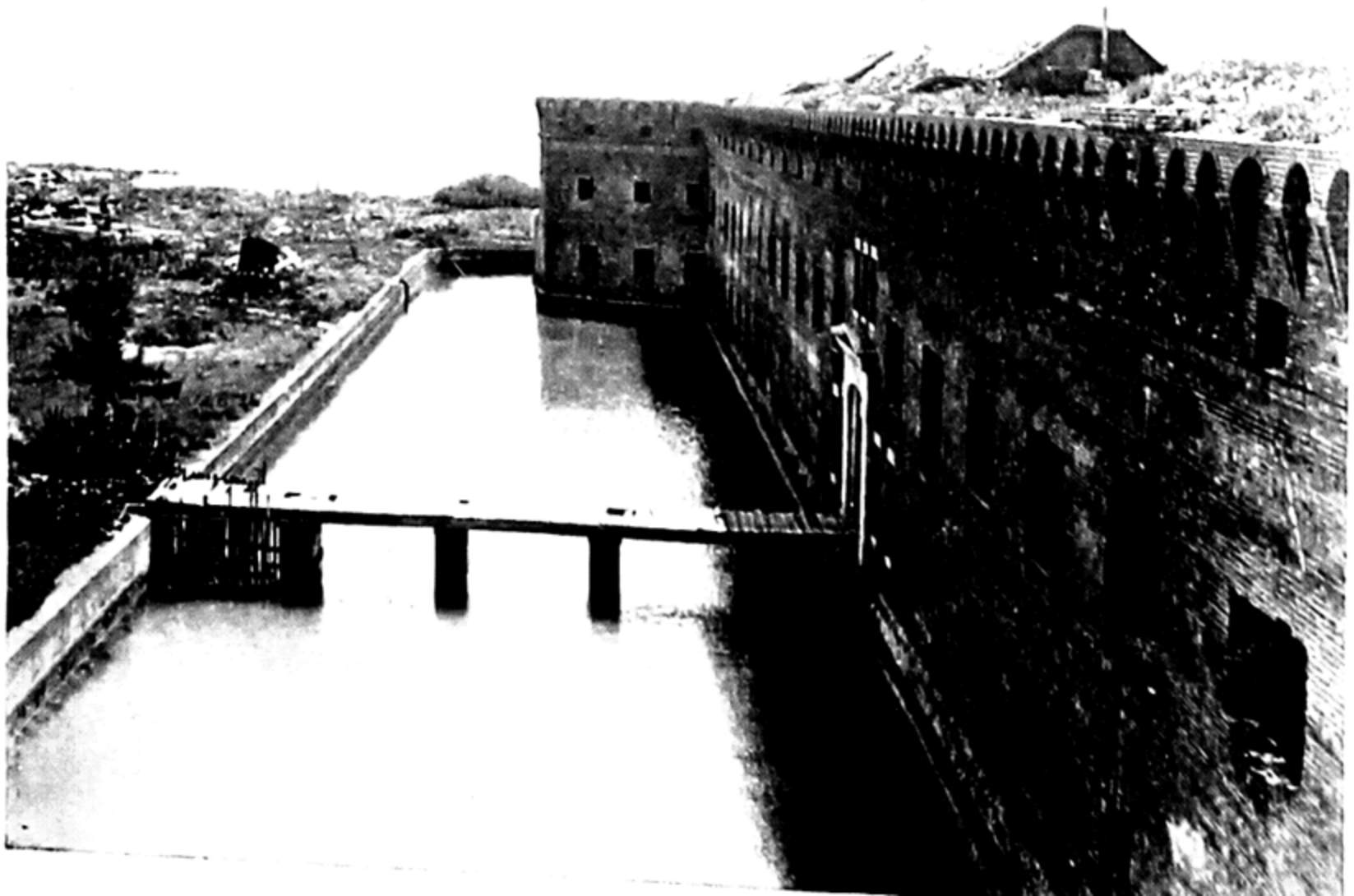


FIGURE 3 – *The moat, Fort Jefferson, Tortugas Islands, Gulf of Mexico.*



FIGURE 4 (*left*) – *Starfish collected by tangles from American oyster bed.*

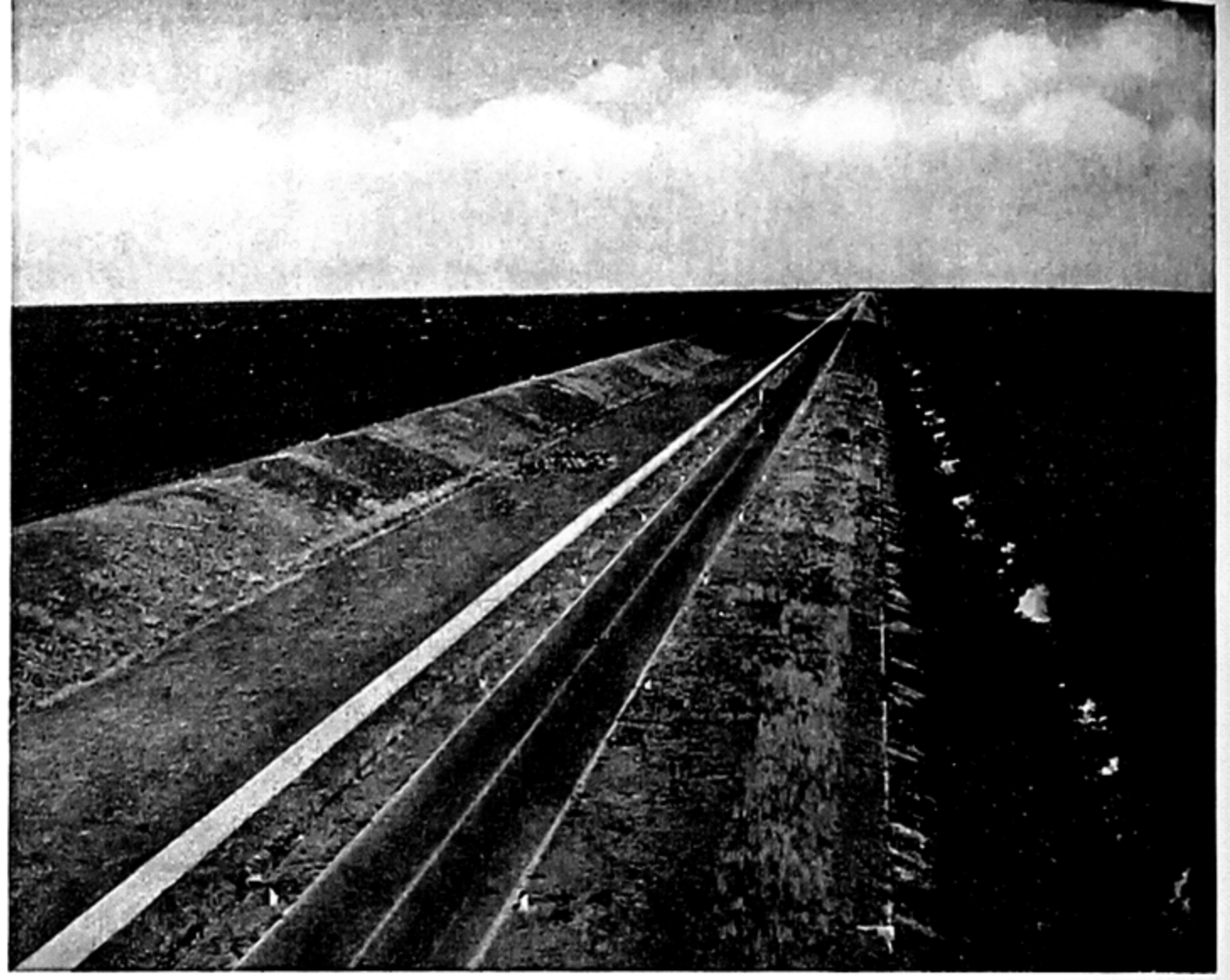


FIGURE 5 – *Zuider Zee dyke.*

Before this dyke was completed in 1932 *a thorough ecological survey was made of the region enclosed by it. Subsequent changes in both the environment and the population have been closely followed. The results of this conversion of a wide area of saline water into an inland lake have proved of great theoretical and practical importance.*

increased in both numbers and size. In the period between the wars much of the scientific activity of the Ministry of Fisheries was devoted to working out and testing possible remedies for overfishing. This was the more necessary because as the years passed the effects of overfishing again became obvious. To take but one example of many cited by Dr E. S. Russell in his book *The Overfishing Problem*: the landings of haddock per day's fishing by English steam trawlers in the North Sea were 7·8 cwt. in 1906; this fell to 4·6 cwt. in 1914, rose to 15·8 in 1919, and had descended again to only 2·6 cwt. in 1937 (figure 6).

One obvious method of control is to enlarge the mesh of the vast trawl nets which annually sweep over practically the entire productive surface of the fishing grounds. This would enable the smaller fish to escape for further growth, and possibly reproduction, before capture. Another, more far-reaching, measure is to limit fishing. This demands a wide knowledge of the natural reproductivity of the fish. Unlike the marine mammals, with their annual or biennial production of one calf, fish produce vast numbers of eggs annually, of which only a few reach maturity. Food, though abundant, is not infinite, and growth is checked owing to intense competition. In other words, a certain degree of fishing is definitely helpful. It reduces competition and enables more fish to attain a large size. But clearly too intensive fishing has the reverse effect. It is a question of knowing exactly how much can be taken out with safety, so that man may obtain a rich harvest without adversely affecting natural stocks. It is actually not only more economical to fish with fewer vessels but the yield may in fact be greater than if too many are employed and the effects of overfishing produced.

Despite the size and obscurity of the fishing grounds, the basic facts concerning the productivity of the chief north Atlantic food fishes are known. This is due to the labours of the scientific staffs of the English and Scottish fishery services and those of the other maritime countries of western Europe. All normally work in close co-operation through the International Council for the Exploration of the Sea. It is now possible to formulate measures of control which, when aided

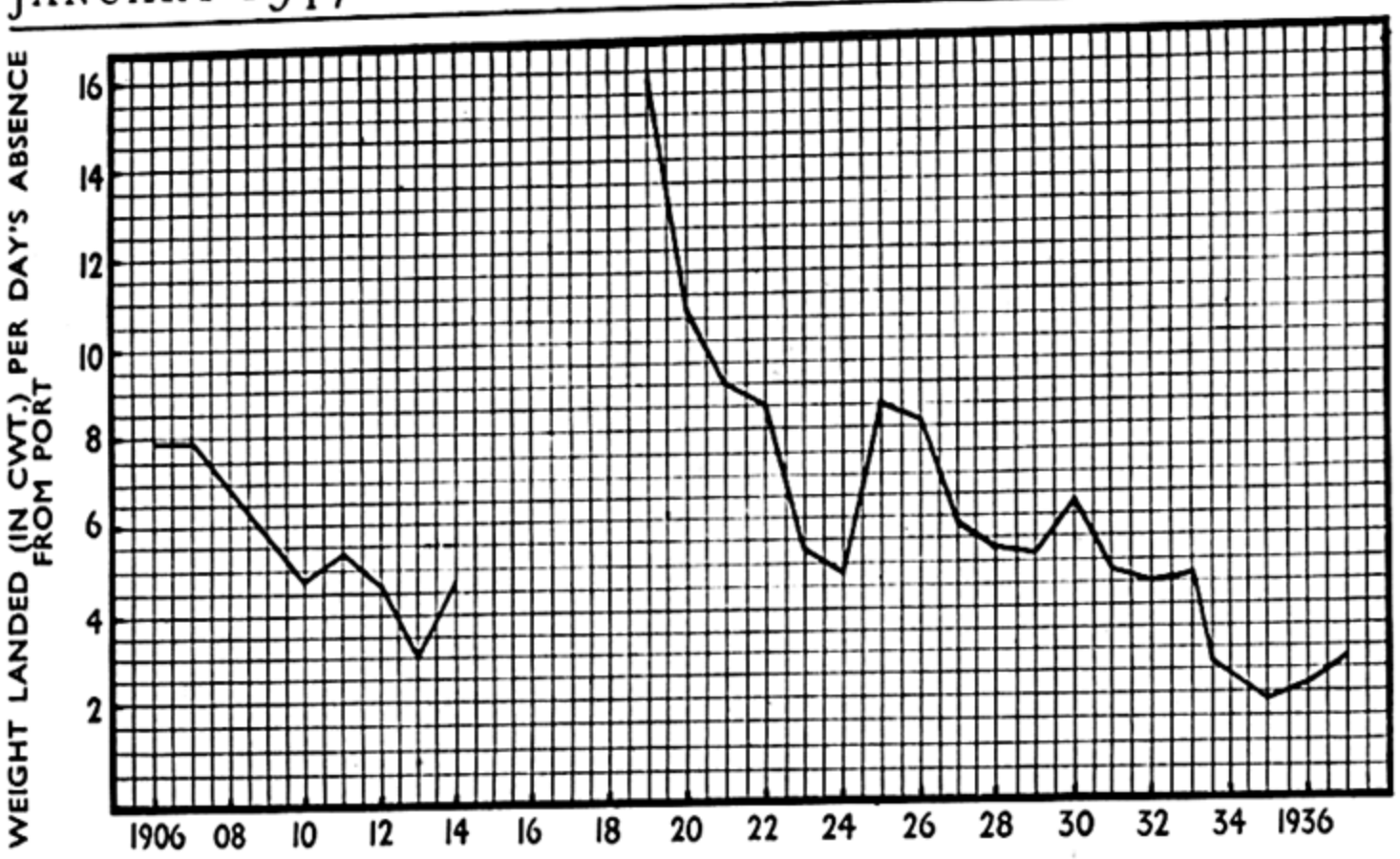


FIGURE 6 – *Graph showing weight (in cwt.) of haddock landed per day's absence by English steam trawlers in the North Sea. The effect of overfishing before and after the* 1914–18 *war, marked by the break in the graph, is well shown.*
(*Data from* The Overfishing Problem, *by E. S. Russell.*)

by continuous scientific supervision, will permit a rational exploitation of the fishing grounds. How successful such action may be is well shown by the result of treaties made between the United States and Canada in 1924 and 1930, and renewed in 1937, for the control of the Pacific halibut fishery, in which both countries are interested. An international fisheries commission was set up, and the fishery, which had undergone catastrophic decline, has recovered to a striking extent after limitation of fishing. In such rapid recovery we see the result of the great fecundity of fish. Populations of whales or seals may take a century to recover fully after too intensive hunting; those of fish will recover in a much shorter time.

Today, after the second close season imposed by war within a generation, there is clearly an opportunity for conserving the now well-stocked fishing grounds of western Europe. The British Government is certainly of this opinion. At its invitation an international overfishing conference was held in London not long after the end of the war. Representatives of all the maritime nations of western Europe except Germany attended, and considered the possibility of agreeing on measures for regulating fishing in the North Sea and adjacent areas. With the needs of starving populations constantly in mind far-reaching decisions could hardly be expected, but agreement was reached on an increase in the size of the mesh of trawl nets and also on size limits for the twelve most important bottom-living food fishes. Limitation of the tonnage of the fishing fleets of the different countries, which was proposed by Great Britain, was not accepted, but the reality of the problem of overfishing was realized to the extent that an advisory committee was appointed to study the matter and propose suitable regulations for the prevention of overfishing in the North Sea and adjacent areas. There is thus some real ground for hope that in the future the fisheries of Europe may, like those of the north Pacific, pass from an era of over-reaching greed to one of rational exploitation based on conservation of the stocks.

Aquiculture, or the cultivation of aquatic life, has been conducted on a very limited scale compared with agriculture. With the exception of some cultivation in Japan of seaweeds from which agar is obtained, it is, moreover, restricted to animals. Its greatest, and by no means negligible, triumph has lain in the cultivation of oysters and other bivalves.

The aim of aquiculture is to increase some part of the population, either in numbers or in size of individuals. This may be done by improving their chances of survival, by transplanting them to regions where food is more abundant, or by increasing the fertility of confined waters. Although there is evidence that the Romans practised crude methods of oyster cultivation in Lake Fusaro and elsewhere, modern cultivation may be said to date from the work of Costé on the French oyster beds. These one-time prolific areas became progressively more depleted as a result of increasing demands from the growing industrial cities during the middle of the last century. Costé realized the fundamental fact that the oyster produces immense numbers of free-swimming larvae, but that only a minute fraction of these find the requisite clean, hard surface for settlement when they sink to the bottom. From his suggestions and experiments arose the modern method of putting out 'collectors,' consisting of half-cylindrical roofing tiles encrusted with lime and sand, in the early summer, when the oysters are ready to spawn. In this way millions of oyster 'spat' find surface for settlement. Costé further

realized the need for protection. After some months of growth, the young oysters are flaked off the tiles and transferred to 'ambulances,' where they are protected by wire netting from their numerous enemies such as crabs, starfish, rays, and marine snails. Later still the oysters are laid out on extensive parks, from which intruders are removed at low tide. Today the vast area of these parks around the shallow, almost land-locked bay of Arcachon, and in other regions of the French coast, are evidence of a flourishing industry. The French also found that oysters would grow and 'fatten' in areas where they will not necessarily breed, and began to transplant oysters into shallow lagoons or 'claires,' particularly around Marennes. In these warm waters the microscopic suspended plant life, or phytoplankton, on which the oysters feed increases rapidly. By such methods a highly organized and immensely productive oyster industry has been built up along the Atlantic coasts of France.

Similar methods, involving provision of settling surface, removal of pests, and transplantation to better feeding grounds, have been developed in many other countries, especially the United States. In the Delaware River, for instance, a natural breeding area some distance up the estuary is maintained, and a collecting surface, in this case consisting of masses of clean oyster shells spread loose or in wire-netting bags, is provided. These shells are later dredged up, the young oysters separated, and a proportion laid on planting beds nearer the sea, where they rapidly grow. The beds are regularly swept with wide-spreading cotton tangles (figure 4) in which the invading starfish are collected in millions, while continuous warfare is waged against other pests. The output of this one oyster fishery runs into some four hundred millions annually.

Along stretches of the Atlantic coast the French also cultivate mussels on long fences of piles and wattling driven into the mud flats. This *bouchot* system was introduced by an Irishman named Walton, who was the sole survivor from a small vessel wrecked in 1235 in the Anse de l'Aiguillon. On the muddy shores of this shallow bay, widely exposed at low tide, he is said to have driven stakes for the attachment of roughly woven grass nets in which he hoped to snare sea birds. He soon found that his nets became covered with mussels, which grew much larger than those on the shore and which proved an excellent source of food. He then took to planting stakes with interwoven twigs between them and so established the simple form of cultivation which still persists.

Modern examples of successful cultivation of bivalves include the unique pearl shell farm at Dongonab in the Red Sea, developed by the late Dr C. Crossland from 1905 until 1923, when a decline in the price of pearl shell caused its abandonment, and the culture pearl industry in Japan. Small beads which form the nucleus of future pearls are enclosed within pieces of the shell-forming tissues of a pearl oyster, and the whole, by a delicate operation, is grafted into the tissues of an intact oyster. A very different animal, the commercial sponge, offers possibilities to the cultivator. It grows attached like a plant, and cuttings may be made which will round off and grow under suitable conditions.

Transplantation of marine animals over great distances raises much greater problems than does that of terrestrial animals. If climate and food are suitable, many domestic and other animals may flourish in the southern hemisphere or in North America as well as, or even better than, they did in their original home in the Old World. Fresh-water fishes may also be transported successfully, as the teeming populations of trout and other fish introduced into the rivers and lakes of New Zealand bear witness. But with marine fish there is the additional factor of spawning migrations. In general, fish grow on their feeding grounds but then migrate against the prevailing currents to spawning areas characterized by very sharply defined physical and chemical conditions. From these the small, surface-dwelling larvae are carried passively back by the currents to the adult feeding grounds, sometimes by way of 'nursery' areas. Thus, though an adult fish may feed and grow in new surroundings, the whole complex mechanism of spawning migrations is upset, and the animals fail to establish themselves. Attempts to introduce herring into New Zealand waters failed probably for this reason. Atlantic salmon, successfully introduced into the rivers, apparently failed to find their way back to the rivers where they must spawn after feeding and growing in the sea.

On the other hand, transplantation over limited distances is possible. Marked plaice have been transplanted from coastal waters to the rich feeding grounds of the Dogger Bank and have there grown much faster than similar animals on the original grounds. The Danes have successfully transplanted small plaice from the crowded waters of the North Sea to the richer feeding grounds of the Limfjord.

It is also possible to transplant some marine

invertebrates which live and spawn in the same place, usually in shallow water. Oysters and other bivalves are normally 'relayed' on a large scale, although attempts to establish lobsters, which have a more complicated life-history, into New Zealand waters have failed. In Great Britain, where the population of 'native' oysters has greatly declined, young or 'seed' oysters have been purchased from France or the United States. Some of those from France have been of the same species as the 'native,' *Ostrea edulis*, but many have been Portuguese oysters, *O. angulata*, which colonized the southern parts of the French Atlantic coast during the past half-century. This oyster grows well on British beds but never spawns, and so can never become established here. It is indeed the spawning temperature, rather than the temperature at which the adult can live, that largely controls the distribution of marine invertebrates. *Ostrea edulis* spawns when the temperature reaches about 15° C, but *O. angulata* does not spawn until 20° C, which is not attained round our coasts. The same difficulty was found when the Japanese oyster, *O. gigas*, was introduced along the Pacific coasts of North America to replace the smaller local species. The temperature is rarely high enough to permit natural spawning, but some success was achieved in the summer months by placing the oysters in floats where the water reached a higher temperature than on the bottom. Later, successful use was made of discoveries by Dr P. S. Galtsoff of the United States Bureau of Fisheries, who found that oysters will breed at lower temperatures if stimulated by the presence of their own genital products in the water. In Vancouver, the Japanese oyster (figure 2) has been regularly induced to spawn by pouring suspensions of ripe egg and sperm, obtained from the sheds where oysters are opened and canned, over the beds at the height of the summer.

So far as we have discussed it, cultivation in the sea consists of ensuring high survival rate of certain stocks in areas where food is abundant. Increase in available food, as produced on land by the use of fertilizers, is still in the experimental stage in aquiculture. The 'fattening' of oysters in the *claires* at Marennes is due to the enrichment of the water by seepage of nutrient salts from the land, the rich microscopic flora so ensured forming food for the oysters. In limited masses of water, fertilization by addition of nutrient salts containing available nitrogen and phosphorus is feasible, and initial experiments by Norwegian and Danish biologists have revealed significant increases in plant and animal life. Similar experiments, aimed at an eventual enrichment of the local stocks of fish, have been carried out during recent years in small lochs along the west coast of Scotland.

The dispersal of the fauna of the land by the activities of man is in no way paralleled in the sea. Some of the reasons for this, such as the association of breeding migrations in fish with ocean currents, and the influence of temperature on the breeding of many marine animals, have been noted. Nevertheless species have been carried to new areas either deliberately, as in the case of the oysters, or else accidentally. When American oysters were relaid on British beds they were accompanied by the slipper limpet, *Crepidula*. This was first noted in the eighties of last century and now extends from the Humber round the south coast as far as Dorset. Unlike the species of oyster which it accompanied here, it is able to breed within the range of temperature found around our coasts and has firmly established itself. It is now a major pest on many British oyster beds. Some twenty years ago it was found on the coasts of Holland, where it had apparently been transported across the North Sea attached to floating wreckage or possibly seaweed. Within ten years it had become a serious pest there also, and had also spread north to the coasts of Germany and Denmark. During the hard years of the recent war the Dutch were driven to utilize this previously unwelcome visitor as a source of human food.

There remain to be mentioned the effects of major engineering works on marine life. The author was first struck by these during a visit to the Carnegie Marine Biological Laboratory on the Tortugas Islands in the Gulf of Mexico. On one of the sandy coral cays arises the immense brick erection of Fort Jefferson, now derelict (figure 3). This is surrounded by a moat which was originally in free communication with the sea and in which became established a representative sample of corals and other marine organisms. In 1919, hurricane seas breached the moat, sand and debris were carried in, and free circulation ceased: it became a sediment trap. In 1934 the fauna of the moat was very different from that when the sea had free access. Only those organisms which could withstand silty conditions survived, and these included only one out of originally seven species of corals, namely *Siderastrea radians*. But the most noteworthy fact was that many of these colonies had become more rounded and had

changed in skeletal form; in this way they had become capable of living in water where there was a continuous fall of sediment.

One of the greatest feats of marine engineering was the cutting of the Suez Canal (figure 7). In 1924, fifty-five years after the canal was opened, the fauna was studied by a Cambridge University expedition under Professor H. Munro Fox. The greatest barrier to the migration of animals through the canal is the high salinity of the Bitter Lakes, originally a dry valley but with salty deposits resulting from the drying up of a former northward extension of the waters of the Gulf of Suez. To a less extent the narrowness of the canal proper, and the stirring up of water in it by the passage of boats, affect large and small animals respectively. But despite these factors and the high temperature of the shallow water, there is now a representative marine fauna in the waters of the canal and its lakes. The animals are predominantly Red Sea species, because powerful currents flow from the Red Sea into the Bitter Lakes, while there is a slow current from there into the Mediterranean for ten months of the year. Only in fish are Mediterranean species well represented, because these move independently of currents. The invertebrate animals are distributed mainly during the drifting planktonic stage of the life-history and so are at the mercy of prevailing currents. Gradually, representatives of the Indian Ocean fauna are passing through into the Mediterranean, where two of them, a pearl oyster and a swimming crab, are now firmly established.

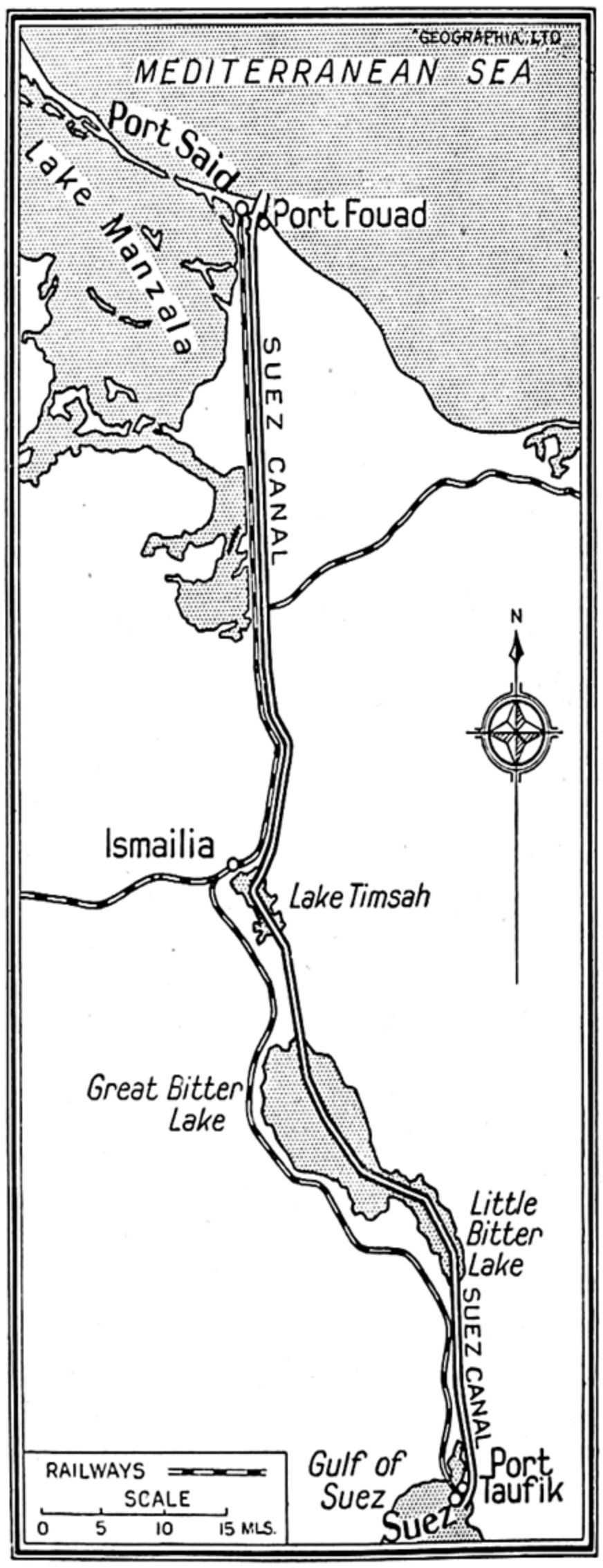


FIGURE 7 – *The Suez Canal.*

The Dutch, in the latest and greatest of their battles with the sea, completed a great dyke (figure 5) across the mouth of the Zuider Zee in June 1932. By so doing they converted a wide area of saline water into a great inland lake. Before the dyke was finished a thorough survey of the animals and plants within the Zuider Zee was made, and subsequent changes in both the environment and the population were closely followed. Originally the latter consisted of a somewhat restricted though essentially marine community, but included a number of endemic species of both plants and animals. Decrease in salinity was accompanied by rise in nutrient salts and so in basic fertility, and there was a widespread change in the fauna and flora. Purely marine species, such as herring, anchovies, plaice, mussels, cockles, and crabs, and also a seal colony on the island of Urk, all disappeared. Porpoises were asphyxiated under the ice which formed on the now fresh water. Brackish-water or estuarine species, notably the solitary endemic crab, maintained themselves to some extent, but fresh water forms which migrated down from the rivers became dominant within two years after the completion of the dyke. These included bass and carp among fish, many fresh-water plants, and also invertebrates such as the harlequin fly, *Chironomus*, which breeds in water. This became so numerous in the initial absence of enemies, that the hordes of flies arising from the water blocked the radiators of cars driving over the dyke.

After the repair of damage suffered during the war, the eventual outcome of this major change brought about by the activities of man will be the conversion of a shallow arm of the sea into a restricted and reed-bordered lake. This will be rich in fresh-water life but will probably contain a few curious remains as sole evidence of its original saline character.

Sydney Young, 1857–1937

J. TIMMERMANS

The preparation of organic compounds of a very high degree of purity is of great practical and theoretical importance. To the experimentalist Sydney Young we owe both recognition of the significance of such substances and the development of elegant new practical methods of obtaining them. Young's eminently reliable work influenced that of scientists in many countries and especially in Belgium, where there was already a well-established tradition in the preparation of pure organic compounds for stoichiometric and other studies.

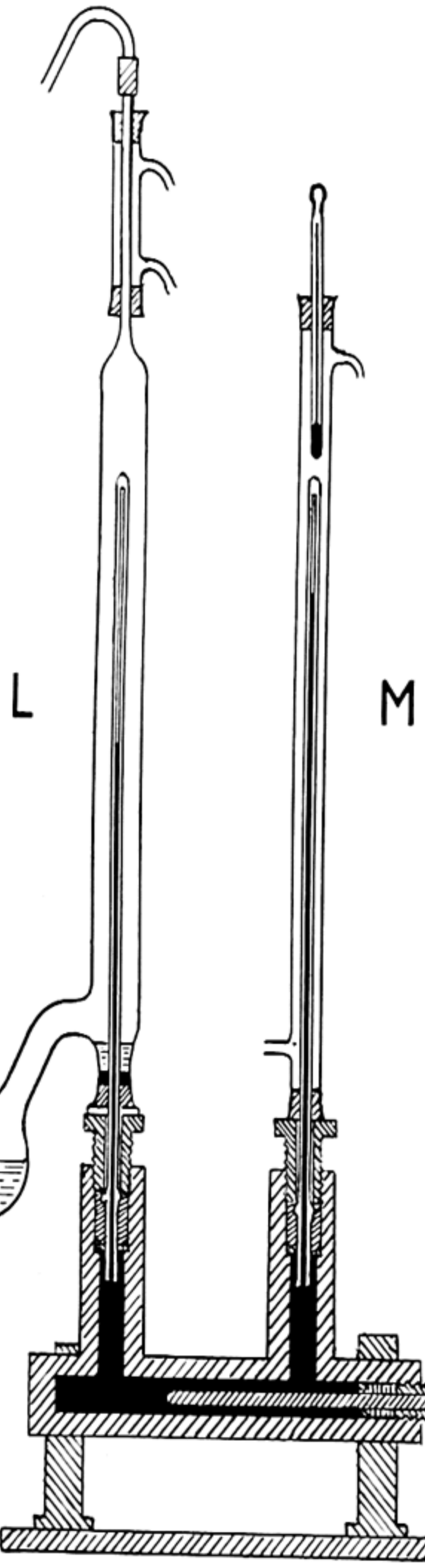
Gas chemistry has always held a place of honour in Great Britain, where much fundamental research on gases has been done. The names of Boyle, Hales, Priestley, Dalton, Cavendish, Davy, Faraday, Andrews, Dewar, and Ramsay immediately spring to one's mind in connection with research in this field. These scientists will always be remembered for the originality of their work. After the early explorers who daringly advance into the unknown come the settlers who take possession of the land and occupy it permanently. In the realm of science this second generation is represented by the experimental scientists whose aim is to establish a precise measuring technique. The reputation of these meticulous workers is more slowly established because their work is less spectacular, but with the passing of time the importance of such investigations as an indestructible basis for further progress becomes apparent. Sydney Young is an important representative of this class of scientific worker—critical rather than creative, but eminently reliable.



FIGURE 1 – *Sydney Young.*

Young, a Lancashire man, studied under Roscoe and Schorlemmer at Owens College, Manchester, and under Fittig at Strasbourg. He obtained his degree as Doctor of Science in 1883, while working with Ramsay at University College, London, where he graduated in 1880. In 1887 he succeeded Ramsay as Professor of Chemistry at University College, Bristol, a position which he occupied for the next fifteen years: this was the most fruitful period of his scientific career. In 1903, at the age of 46, he became Professor of Chemistry at Trinity College, Dublin. There the burden of work connected with teaching and examinations left him time for little more than theoretical interpretations of his earlier experiments. He was chairman of the chemistry section at the Annual Meeting of the British Association at Cambridge in 1904, chairman of the Royal Irish Academy, and a Fellow of the Royal Society.

This is not the place for a detailed chronological account of Young's researches or of the papers he published. This may be found in the excellent biographical studies made by his successor at Bristol, Professor Francis Francis (*Journal of the Chemical Society*, 1937, 1332), and by his old pupil in Dublin, Dr W. R. G. Atkins (*Royal Society Obituary Notices*, 1937, **2**, 371). Here it will suffice to give a general outline of the activities of the great experimentalist. There was a remarkable uniformity in his career; he devoted some twenty years of his life to a study of the thermodynamic properties of, and the heterogeneous equilibria between, about thirty highly purified organic compounds. The results of these researches appeared in 1908 in his book *Stoichiometry*. In preparing the pure substances required for his researches he improved the existing methods and apparatus used for fractional distillation. His observations



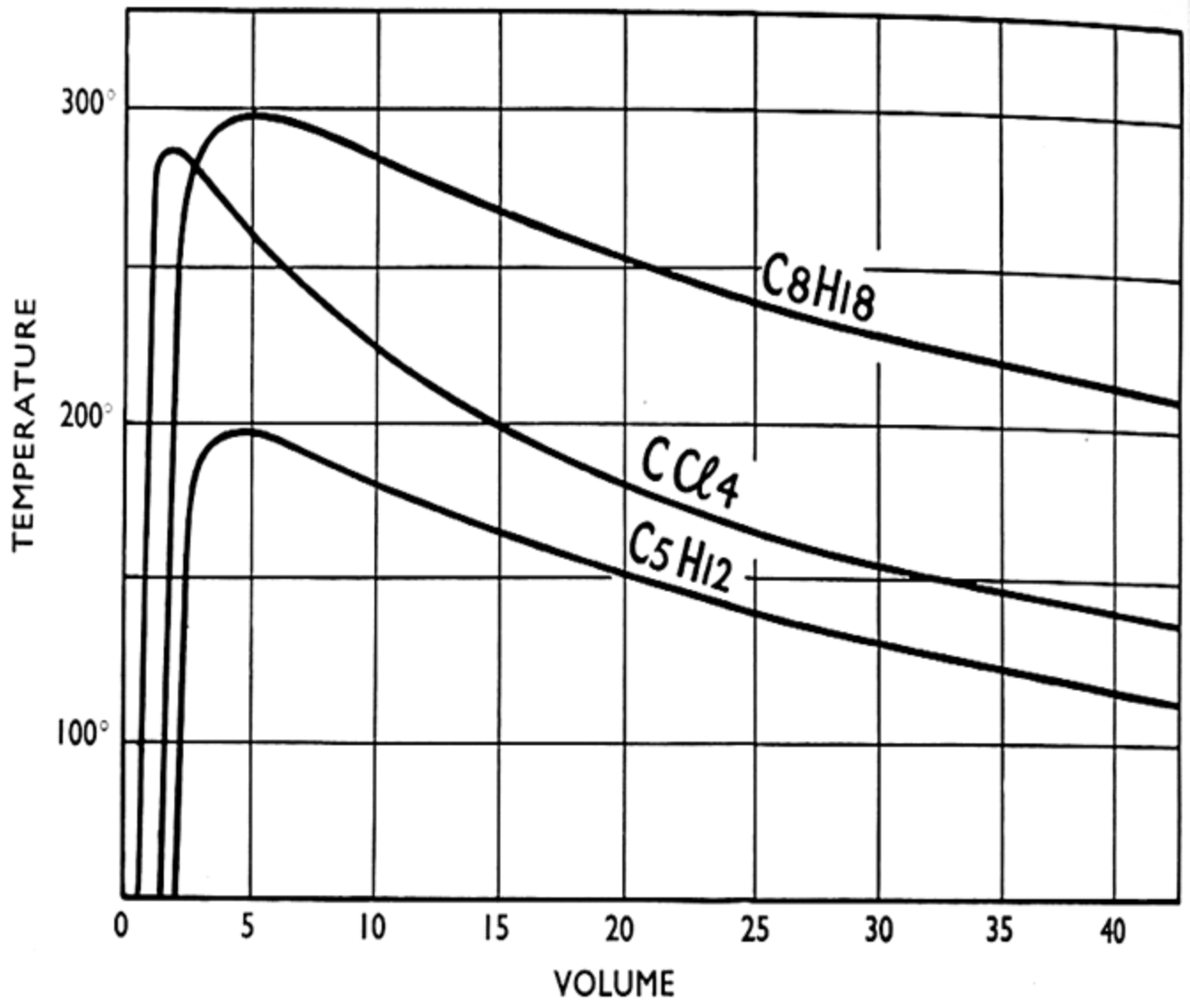
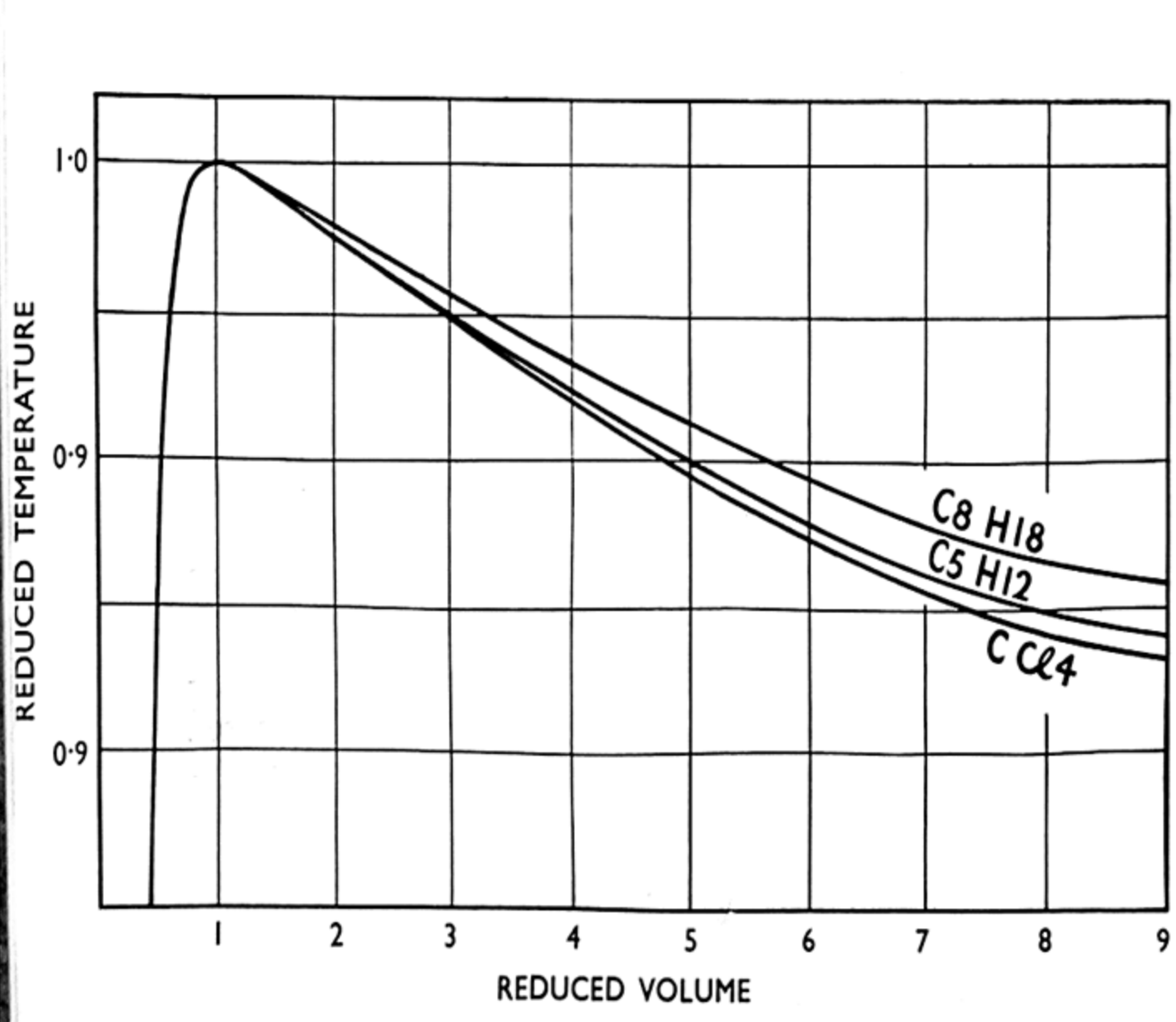


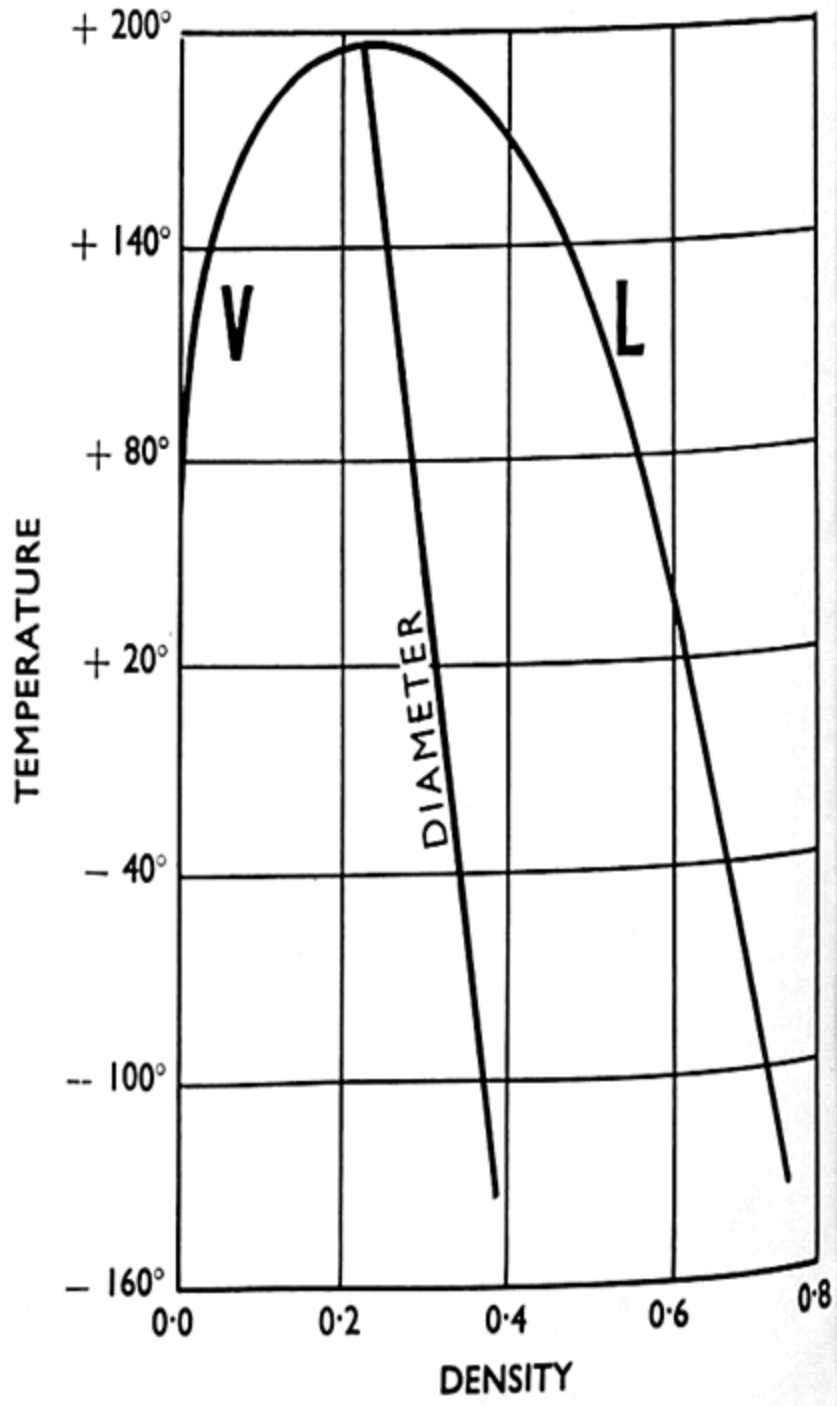
FIGURE 2 (*left*) – *Ramsay-Young apparatus for studying the equation of state. L = reaction tube. M = gas manometer.*

FIGURE 3 (*above*) – *Specific volumes of liquid and saturated vapour in c.c. and temperature in degrees Centigrade (orthobaric volumes).*

FIGURE 4 (*below, left*) – *Reduced orthobaric volumes of the same substances expressed in terms of critical volume and critical temperature.*

FIGURE 5 (*below, right*) – *Orthobaric density of n-pentane, illustrating the law of rectilinear diameters* (*see page* 13). *V represents the saturated vapour phase and L the liquid.*





in this field were embodied in a second treatise, *Distillation, Principles and Processes*, of which the first edition was published in 1922.

Young's first experiments on heterogeneous equilibria were suggested to him by Roscoe and carried out under the supervision of Ramsay. Their object was to examine the behaviour of saturated vapour, crystal, and liquid phases in the neighbourhood of the triple point. Shortly afterwards, however, he specialized in precise determinations of the thermal constants, density, vapour pressure, and critical constants of a great number of organic substances, such as acetic acid, benzene and its halogenated derivatives, cyclohexane, paraffins, carbon tetrachloride, alcohols, and esters of the fatty acids. These researches established for Young a reputation for impeccable precision. As his means were limited he built his own glass apparatus—these are models of ingenuity and simplicity (figure 2). In making determinations of temperature, specific volume, and saturated vapour pressure he not only took the greatest care in making all the corrections needed for the high accuracy he achieved, but managed to avoid making his technique unnecessarily complicated. His mastery of technique is illustrated by his use of ordinary thermometers, graduated in degrees on the stem, for his extremely precise measurements of temperature. These thermometers were, however, prepared with great care. To avoid variations in the zero point they were annealed in a bath of boiling naphthalene. He himself made the table of corrections for all parts of the scale by suspending the thermometer in vapour from pure boiling liquids, a method still regarded as giving reliable standards. The accuracy of his results is such that even after fifty years they remain unquestioned.

Young's magnificent work in the determination of constants is important not only because it gives so many precise data relating to fundamental experiments, but because it is of significance in assessing the validity of the equation of van der Waals. Young was able to demonstrate that, generally speaking, his quantitative results conformed well with theory at every point, but that certain numerical coefficients had to be altered. For example, the critical coefficient $D_{cr.}/D_{calc.}$, where $D_{calc.}$ is the density (specific volume) obtained by applying the laws of perfect gases at the critical temperature and pressure, was assigned the value 2·7 by van der Waals, whereas observation gives the value 3·8. The theory of corresponding states is more accurate than the equation of van der Waals from which it is derived (see figures 3 and 4). Young also tested very carefully the so-called law of rectilinear diameters, which states that if the mean of the densities of the liquid and saturated vapour at any temperature be plotted against the temperature, the points so obtained will lie on a straight line. In only one case, that of normal pentane, was the law exactly followed; the curves for all the other liquids examined showed a slight but distinct curvature. (See figure 5.)

The care taken by Young in the execution of his very precise measurements places him on the level of physicists like Regnault. His pioneering work lay in the preparation of organic compounds in a state of high purity, for his exact determinations of the critical constants of a large number of substances showed him how sensitive these constants are to traces of impurities. Before his time only Mendelejeff, using ethyl alcohol, and de Visser, using acetic acid, had demonstrated the possibility of preparing completely homogeneous, anhydrous organic substances characterized by the constancy of their physical properties. Young verified this for a large number of substances, and his success was such that, in the great majority of cases, his values are still accepted as standards today. There again he devised methods of overcoming difficulties which were so simple and effective that they are still used.

His experimental work entailed the determination of the boiling-points of a large number of homologous compounds in various organic series. He was able to demonstrate that on the Kelvin scale the difference (Δ) between the boiling-points, at normal pressures, of two successive members of such series depends only upon the boiling-point of the first member. In general the results conform well with the general formula

$$\Delta = 144{\cdot}86/T^{0{\cdot}0148\sqrt{T}}$$

This is one of the few stoichiometric relationships which have real quantitative significance.

His work on the preparation of pure substances compelled Young to devise improvements in the methods of distillation and in the design of dephlegmators then in use. The 'evaporator still-head' and column of Young and Thomas was the first apparatus which made possible the separation of *n*-pentane (boiling-point 34·5° C) from *iso*pentane (boiling-point 29·0° C), both of which are contained in light petroleum.

To Young also we owe both new experimental methods, and new ways of representing the

resulting data, which have proved of great practical importance in the laboratory and in industry. He discovered large numbers of azeotropic mixtures and pointed out simple methods of determining their composition: this opened a new and very fruitful field of science. He determined the exact composition of some ternary azeotropic mixtures, and his process for the dehydration of ethyl alcohol by elimination of the water in the form of a ternary azeotropic mixture with benzene has been employed in the Kahlbaum works in Germany.

While Young was engaged in this important research during the last decade of the nineteenth century, several other British scientists were also engaged in the study of very pure substances. Perkin was interested on account of his work on magnetic rotatory power, and Thorpe because of his measurements of viscosity. Although Young did not establish a school of his own in England, his work has long influenced foreign scientists, particularly in Belgium and in the United States.

Belgian chemists had a well-established tradition of particularly conscientious work in connection with the preparation of pure substances. This work was originated by Jean Servais Stas, who required perfectly pure materials for his determinations of atomic weights, and by Léon Crismer, who demonstrated the importance of the critical temperature of dissolution as a simple and highly sensitive criterion of purity. Crismer used this test to establish the most efficient methods for completely drying methyl alcohol and its homologues. When Belgian chemists became aware of the work of Young there was a swift development of the techniques necessary for the study of pure organic compounds. Chavanne improved the methods used for the identification of mineral oils of different origins, submitting them to fractional distillation and comparing with synthetic samples the fractions so obtained. The work of Chavanne's pupils is marked by the particular care taken in the purification and identification of organic substances. At the University of Louvain, Louis Henry had always attached great importance to stoichiometric relationships in organic chemistry, a study which involves the use of pure reagents. In this connection, Pierre Bruylants and his school have done brilliant research on density and refractive index in the paraffin series. At Ghent, the work of Frédéric Swarts, to whom we owe the characterization of most known organic compounds of fluorine, is marked by the care taken in the purification of samples used for some of the determinations, notably for measurements of refractive index and heat of combustion.

This combination of favourable circumstances led to the creation in Brussels, in 1921, under the auspices of the Union Internationale de Chimie, of the Bureau of Physico-chemical Standards, where the main physical constants of nearly two hundred of the commonest organic compounds have been accurately determined. It was in Brussels too that Lecat started his chemical researches, now so extensive and fruitful, in the field of azeotropism.

In the United States, departments of the Bureau of Standards in Washington have undertaken, under the guidance of Professor Washburn, some important work on the identification of very pure petroleum hydrocarbons, and on their heats of combustion. Other researches, notably those carried out in California, relating to the measurement of changes in entropy, have necessarily led to the preparation of great numbers of pure organic compounds. In the United States the influence of Young is also felt, though indirectly, through two former students of the University of Brussels. Albert Henne, professor at Columbus University, Ohio, has done fine work on organic compounds of fluorine which combines characteristics of the schools of both Chavanne and Swarts. Georges Callingaert, director of the research department of the Ethyl Gasoline Corporation, Detroit, has successfully undertaken the study of very pure hydrocarbons.

It is thus evident that the example set by Young has started several important schools of research on pure organic compounds. Scientific workers had too long been content to deduce so-called constants from measurements carried out on only approximately purified samples, and there was a manifest discrepancy between the accepted standards of chemical purity and the standards of accurate physical measurement. In the inorganic field it had long been recognized that each definite compound is characterized by physical constants which, provided the process of purification has been properly carried out, are independent of the origin of the sample. The instability of organic substances, together with the difficulty of purifying them and of keeping them pure, led to the belief that this was not so in organic chemistry. It is to Young that we owe the convincing demonstration that a pure organic substance is as precisely defined as one of the elements themselves, and on this rests his main title to fame.

Some applications of optical crystallography

N. H. HARTSHORNE

During the last fifteen or twenty years, the polarizing microscope has proved its worth in the identification and analysis of solid substances, not only in pure science but in industry and technology. By its use, for example, members of a series of closely related compounds may easily be distinguished from one another, the individuals in solid mixtures of salts can be identified, organic stereoisomers may be differentiated, and the nature of the solid phases in such forbidding systems as high-temperature silicate mixtures can be ascertained.

The determination of the optical properties of transparent crystalline substances by means of the polarizing microscope forms, as is well known, the basis of a standard petrological technique for differentiating and identifying the mineral species in rocks. It is perhaps not so well known that this method of identification has also found many useful applications in other fields, notably in general chemical practice and in the study of a variety of natural and industrial products, including refractories, slags, building cements, explosives, plastics, and textile fibres. Several authors [1] have drawn attention to the wide applicability of the method, which is illustrated in the present article. For greater clarity it has been thought desirable also to include an outline of the underlying principles of the method.

Two other crystallographic methods of identification are based respectively on the measurement of characteristic interfacial angles, and the use of X-ray powder spectrograms as 'fingerprints.' The first of these can be applied only to well-formed crystals of individual compounds which are large enough to be mounted on a goniometer. The second method can be directly applied to mixtures, and is particularly useful when the state of division of the material is near, or less than, the limit of microscopic resolution. But where this is not so, it will commonly be found that the optical method is quicker, simpler, and more appropriate. Moreover this method has the advantage that it gives direct information about the texture of the specimen, the form and size of its particles, and, if it is a mixture, the distribution of its ingredients, all of which may be of prime importance in the problem on hand.

The essential features of crystal optics are as follows. Crystals of the cubic system are *isotropic* to light, that is, light passes through them with the same velocity in all directions. Crystals of all other systems are *anisotropic*: their structure and therefore their physical properties, including the velocity of propagation of light, are different in different directions. When a beam of light enters such a crystal, it is in general refracted into two beams which have different velocities and are polarized in planes at right angles to one another. There are, however, certain directions called *optic axes* along which this double refraction does not occur. Tetragonal, hexagonal, and trigonal crystals have one such direction and are therefore termed *uniaxial*; orthorhombic, monoclinic, and triclinic crystals have two, and are termed *biaxial*.

It follows that every section of an anisotropic crystal (except sections normal to an optic axis) has two directions of vibration, corresponding to different refractive indices, along which light entering at normal incidence is constrained to vibrate. In most cases these vibration directions are the same, or nearly the same, for all wavelengths; the refractive indices associated with them vary, of course, with the wavelength.

The maximum and minimum refractive indices of a crystal for a particular wavelength, together with, in the case of biaxial crystals, the index for light travelling along an optic axis, are known as *principal refractive indices*, and are important optical constants characteristic of the substance. In uniaxial crystals, one of these (ω) is the same for all directions of propagation, and the other (ε) is the index which differs most widely from it. In biaxial crystals, the maximum and minimum indices are denoted by γ and α respectively, whilst that for light travelling along an optic axis is denoted by β.

The equipment required for most optical crystallographic work is quite simple, and the set shown in figure 2 is adequate for all normal

problems. The essential item, the polarizing microscope, is a compound microscope fitted with a rotating stage and two nicol prisms (or 'Polaroid' plates in some modern British and American models[1]). The lower nicol (*polarizer*) is fitted below the stage, and the upper one (*analyser*) at some position above the objective. When both nicols are in position and 'crossed,' cubic crystals can be distinguished immediately from anisotropic crystals, since the former remain as dark as the rest of the field in all positions, whilst the latter in most positions exhibit *polarization colours* (if white light is used) but 'extinguish' at intervals of 90° as the stage is rotated. The reasons for these phenomena are that isotropic material has no effect on the vibration direction of the light from the polarizer, but anisotropic crystals resolve this light into a 'fast' and a 'slow' beam, components of which interfere in the analyser. Only part of the spectrum emerges in phase, and so the light seen is coloured. As the stage is rotated, the vibration directions of the crystal become parallel to those of the nicols every 90°, and extinction results because at these positions the crystal does not affect the vibration direction of the light from the polarizer (see figure 1). Observations of the effect of compensators (crystal wedges and plates of known optic orientation and birefringence—see figure 2) on the polarization colour shown by a crystal section enable its 'fast' and 'slow' vibration directions to be found.

By illuminating a crystal between crossed nicols with a strongly convergent beam of light and bringing to a focus rays which have passed through the crystal in parallel directions, an *interference figure* is obtained. This consists in general of a pattern of polarization colours and bands of darkness. A study of the characteristic patterns given by certain sections of the crystal reveals whether it is uniaxial or biaxial, and in the latter case enables the angle between the optic axes to be measured. It is also an important means of determining the orientation of the principal vibration directions (that is, those associated with the principal indices) with respect to the external form of the crystal.

Refractive indices are determined with the polarizing microscope by making use of the fact that when a crystal is immersed in a liquid having the same index, the crystal/liquid boundary disappears. It is therefore only necessary to mount portions of the material in a succession of liquids of known index until one is found in which the crystal border is invisible. The search is facilitated by the fact that the greater the difference between the indices of crystal and liquid, the stronger is the relief in which the former appears, and also by observations of the so-called Becke line. The latter is a bright line of light which appears, under suitable conditions of illumination, just inside the medium of higher index, and (a more certain indication) which moves farther into that medium when the microscope tube is slightly raised. The two indices of a birefringent section may be

[1]Such microscopes are now being produced by Messrs. Cooke, Troughton, and Simms, and by the Spencer Lens Company. The advantages are that a wide aperture may be provided without undue expense, the construction of the microscope is simplified, and the maker is independent of the supply of Iceland spar of optical quality, which is not abundant.

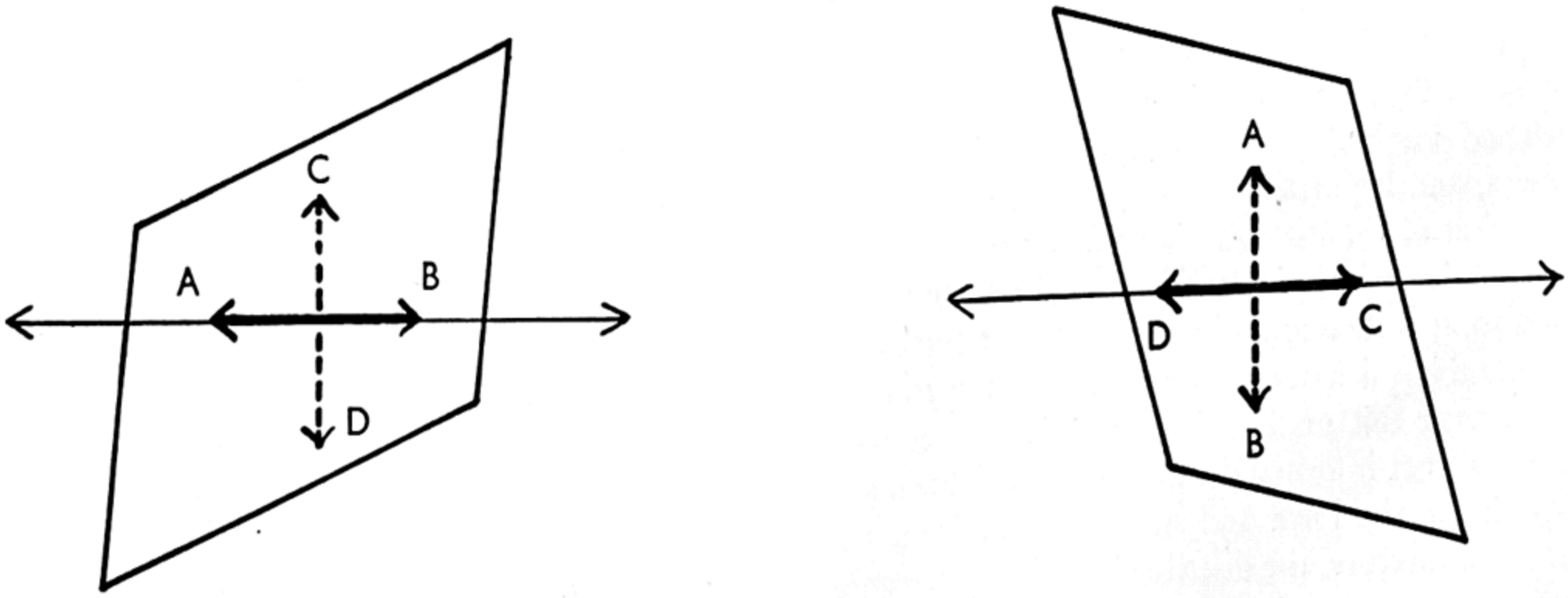


FIGURE 1 – *Isolation of the beams transmitted by a crystal section. In both positions shown the crystal would be 'in extinction' between crossed nicols. The long horizontal arrows represent the vibration direction of the light from the polarizer.*

(a) Vibration direction AB of crystal parallel to vibration direction of light from polarizer; no light vibrating parallel to CD is transmitted.

(b) Crystal turned through 90°. Vibration direction CD of crystal now parallel to vibration direction of light from polarizer; no light vibrating parallel to AB is transmitted.

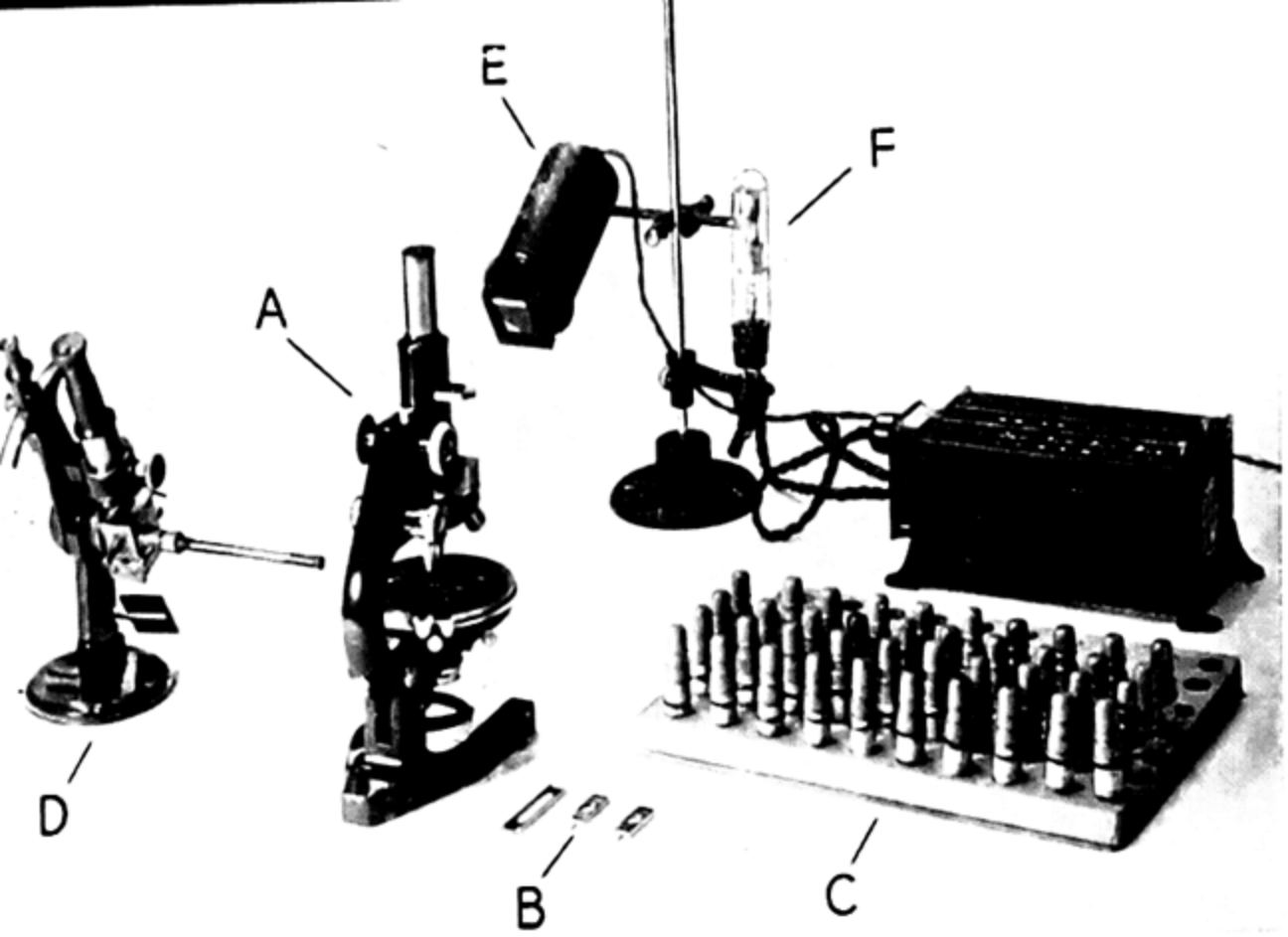
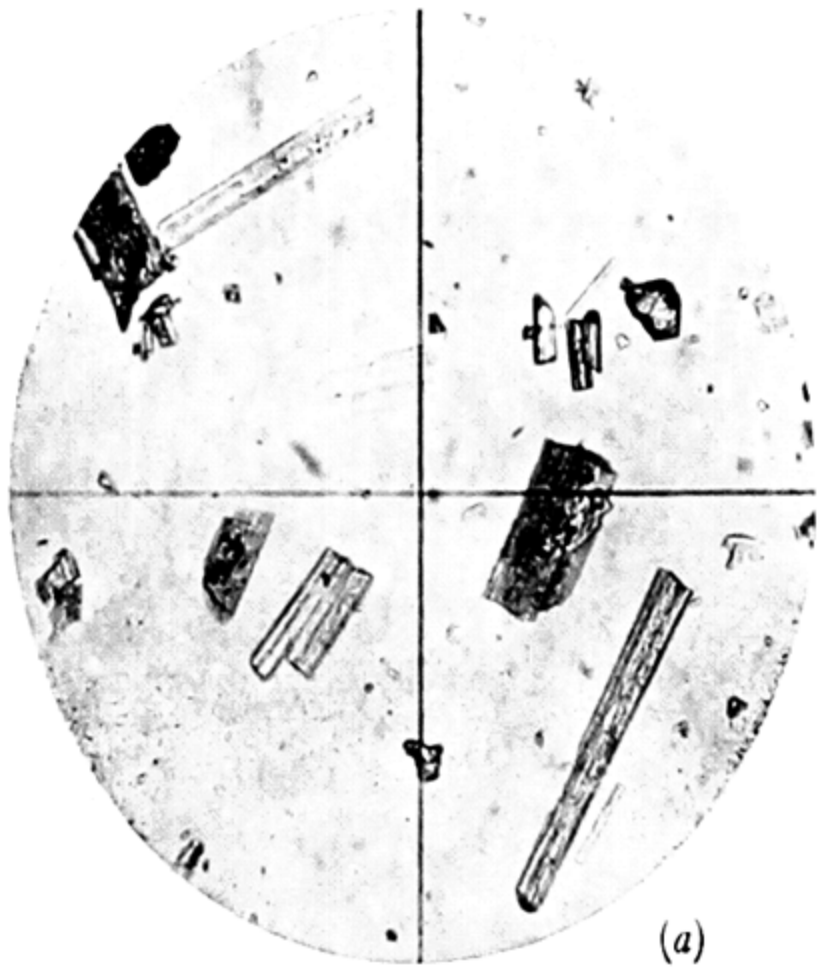


FIGURE 2 (*left*) – *Equipment required for determining optical crystallographic properties.*

A = *Polarizing microscope.*
B = *Compensators (quartz wedge, ¼-wave mica plate, 1-wave gypsum plate).*
C = *Mounting liquids of known refractive index.*
D = *Abbé refractometer for checking values of C.*
E = *Source of white light.*
F = *Sodium lamp.*



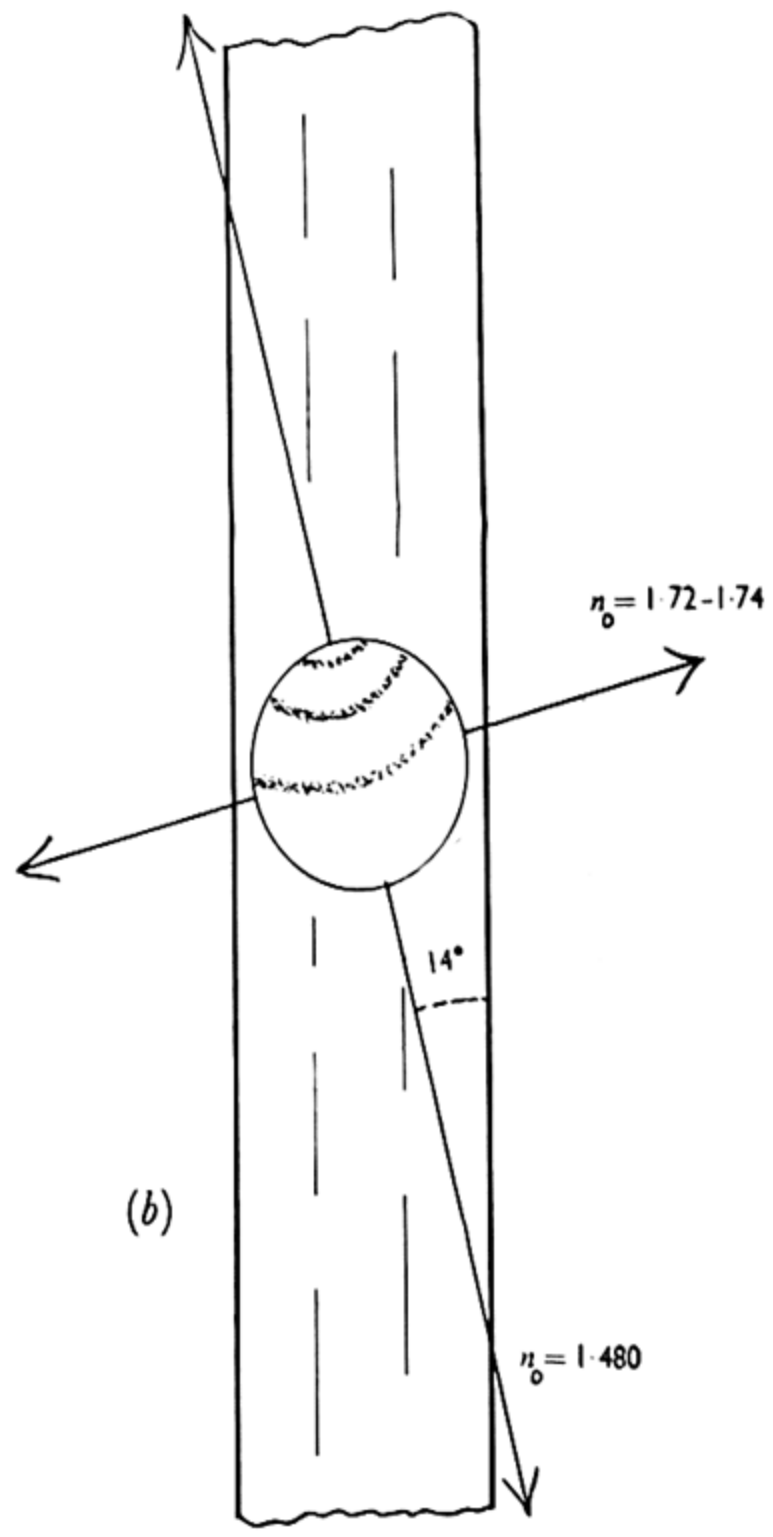


FIGURE 3 – *p-Nitrobromobenzene.*

(a) Mounted in liquid of index 1·494 (D) (× 100) in polarized light vibrating parallel to horizontal cross-hair. Crystals lying nearly parallel to this direction show weak relief, since the index for light vibrating along their length is near that of the liquid. (See (b).)
(b) Optical properties of section presented by crystals in (a).

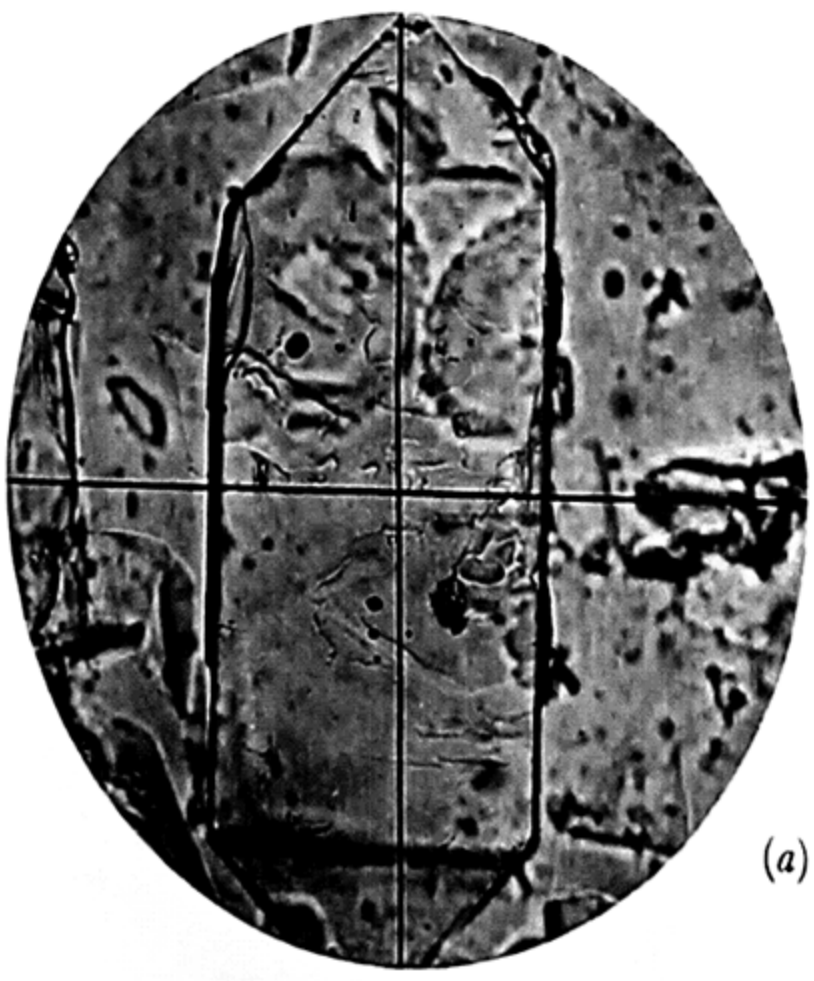
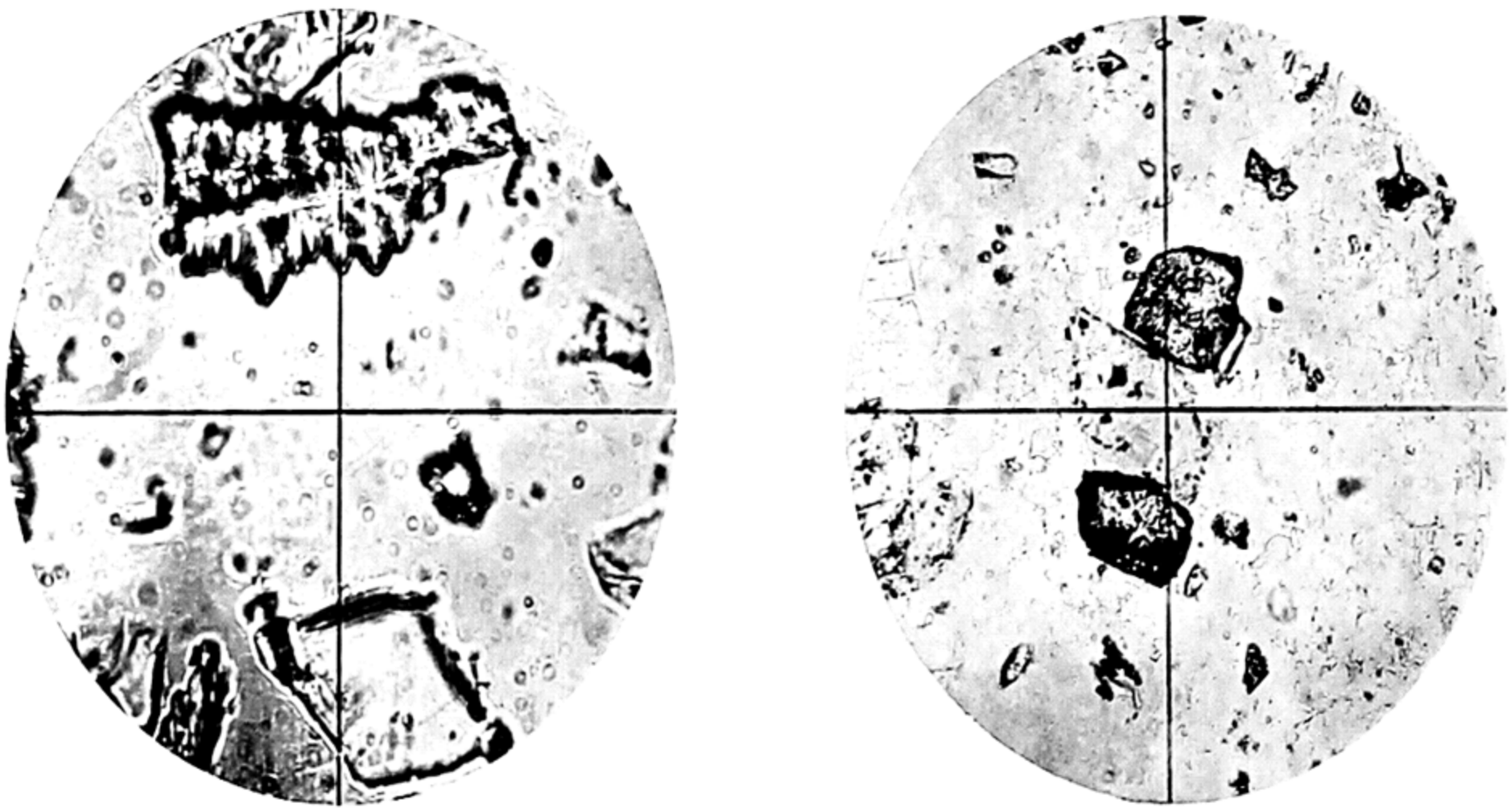


FIGURE 4 – *Crystal of $NH_4H_2PO_4$ mounted in liquid of index 1·531 (D) in polarized light (× 100). Substage diaphragm nearly closed.*

(a) Light vibrating vertically, parallel to the ε (1·479, D) vibration direction. Note strong relief.
(b) Light vibrating horizontally, parallel to the ω (1·525, D) vibration direction. Crystal and liquid are nearly matched.
In both cases note Becke line just outside border of crystal, indicating $n_{liquid} > n_{crystal}$.

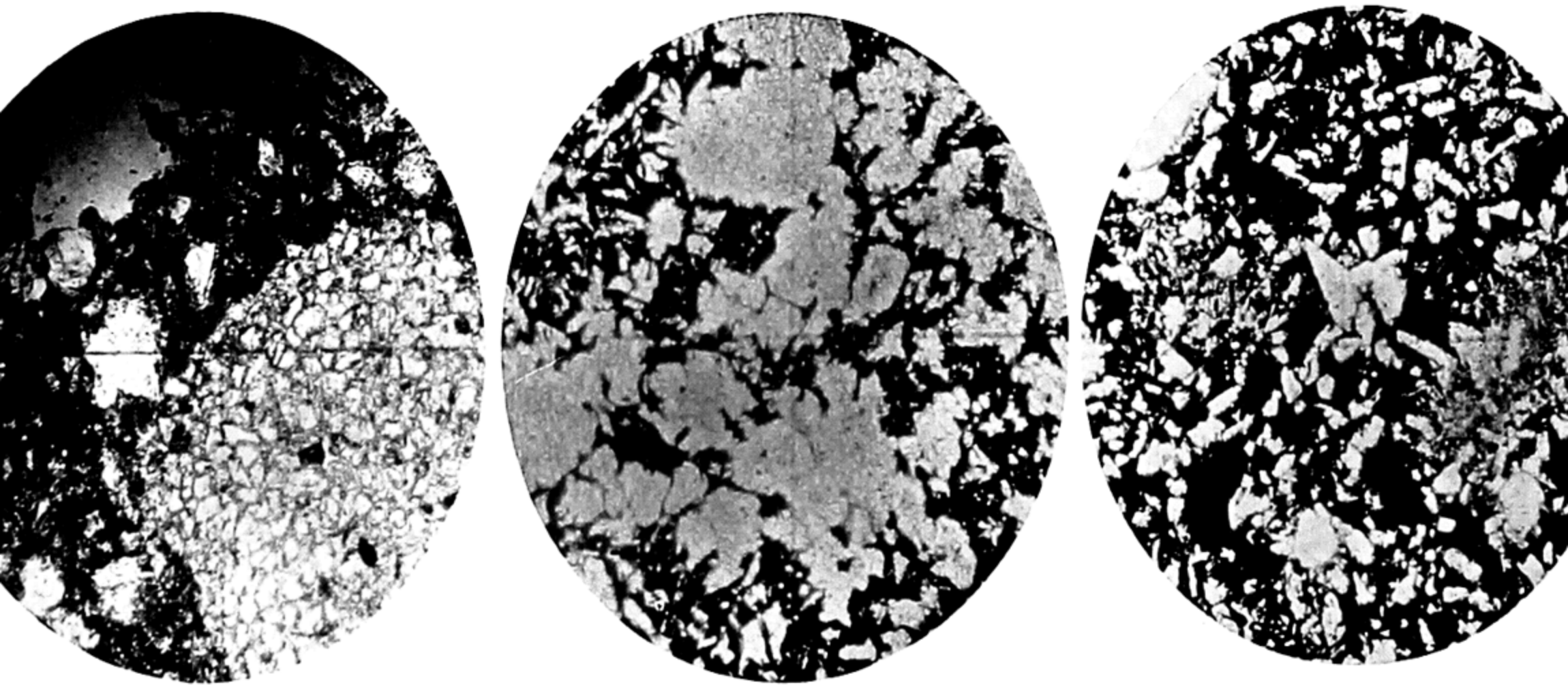


(*a*) (*b*)

FIGURE 5 – *Distinction between salt mixtures having the same ions.*

(*a*) $PbCl_2 + Ba(NO_3)_2$ *in liquid of index* 1·633 (× 480). *Substage diaphragm nearly closed. Dendritic crystal of* $PbCl_2$ (*birefringent,* $n_D = 2{\cdot}199–2{\cdot}260$) *in upper half of figure shows Becke lines inside crystal border. Large crystal of* $Ba(NO_3)_2$ (*isotropic,* $n_D = 1{\cdot}571$) *in lower half of figure shows Becke line outside crystal border.*

(*b*) $Pb(NO_3)_2 + BaCl_2.2H_2O$ *in same liquid* (× 100). *In centre of figure are two large crystals of* $Pb(NO_3)_2$ (*isotropic,* $n_D = 1{\cdot}7815$) *in strong relief, with crystal of* $BaCl_2.2H_2O$ (*birefringent,* $n_D = 1{\cdot}635–1{\cdot}660$) *between. The latter shows in weak relief, since* $n_{liquid} \approx n_{crystal}$.



(*a*) (*b*) (*c*)

FIGURE 6 – *Thin sections of silica brick* (× 50).

(*a*) *Soft-burned brick before use. Light area (lower right) is ganister fragment consisting of unaltered quartz. Remainder largely interstitial material consisting of unaltered quartz grains, with cristobalite and glass.*

(*b*) *After use as roof brick in open-hearth furnace. Inner zone, consisting of isotropic cristobalite (white grains in figure) and magnetite (dark ingredient) from furnace charge.*

(*c*) *Ditto, tridymite zone. Tridymite (white in figure) in typical prisms and 'arrowhead' twins, one of which is seen just above the centre of the figure.*

separately compared in this way with that of the liquid by using polarized light and isolating the two beams as explained in figure 1.

Figure 4 illustrates the application of this method to ammonium dihydrogen phosphate, a uniaxial substance which habitually crystallizes in square prisms with pyramidal ends. These crystals lie on their sides, and in this position they present both of the principal indices, ε being that for light vibrating along the length of the prism, and ω that for the transverse direction.

In such cases the determination of the principal indices is a simple matter. It frequently happens, however, especially with crystals of low symmetry, that the most prominent faces, which determine how the crystals lie on the slide, are parallel to none of the principal vibration directions, and so the indices shown have intermediate values. Simple methods are available for determining the principal indices of such crystals, and also of crystal grains and fragments possessing no characteristic external form which adopt random positions on the slide, but space does not permit of their being described here. It should be said, however, that it is not always necessary to determine the principal indices of a substance in order to identify it. Figure 3 illustrates a case in point. *p*-Nitrobromobenzene habitually crystallizes as shown in (*a*), and nearly all the crystals lie so as to present the optical characters shown in (*b*), which gives the inclination of the vibration directions to the long axis of the crystal, the refractive indices (neither of them a principal one), and, in the central circle, the interference figure. Provided that the substance does not adopt some radically different habit, this combination of optical properties can be used to identify it.

The following examples are only a few of the very many that could be quoted to illustrate the value of the optical method, but they serve to show something of the range of problems covered.

The qualitative chemical analysis of a mixture of salts reveals merely what ions are present. For example, suppose that barium, lead, nitrate, and chloride ions are found. Does the mixture consist of $PbCl_2$ and $Ba(NO_3)_2$, or of $Pb(NO_3)_2$ and $BaCl_2.2H_2O$, or of some other possible variation? A knowledge of their refractive indices and of the fact that the two nitrates are isotropic enables a decision to be reached in a matter of minutes, merely by mounting the mixture in a liquid having an index intermediate between the extreme values shown by the salts and observing the Becke line and the behaviour between crossed nicols (see figure 5).

Some years ago, the author had occasion to examine some specimens of potassium mercuric iodide and ammonium dihydrogen phosphate, the purity of which was in doubt [2]. Under the microscope the former was seen to contain colourless isotropic crystals with a refractive index slightly greater than 1·66. This showed that the impurity was potassium iodide, which is cubic and has an index of 1·67. Associated with the uniaxial phosphate were found fragments which did not show the ω value of this salt, and gave biaxial interference figures. This suggested that the impurity might be the biaxial diammonium salt, and this was confirmed by a determination of the β index. In neither of these cases could the impurity have been identified by chemical analysis.

Numerous examples of the use of the polarizing microscope in organic chemistry have been quoted by Benedict [3]. For instance, in studying the preparation of certain amino acids he was able to save much time by using optical methods of identification (based on data previously obtained by Keenan; see below), particularly in view of the fact that the acids had indefinite melting-points and could not be characterized by this property. A drop of the reaction mixture could be quickly examined with the microscope to see whether in fact it contained the required product, and so no time was wasted in working up the products of unsuccessful runs. Side reactions were also investigated by the same means.

Bennett and his co-workers have used the method as a means of differentiating between organic stereoisomers, a particularly interesting example being the isomeric trithioacetaldehydes [4]. Two isomers only are required by stereoisomeric theory, and an alleged third isomer was found under the polarizing microscope to be a eutectic mixture of these two.

With the objects of demonstrating the value of the optical method in organic chemistry and of adding to the body of published data, a large number of optical crystallographic studies of series of related compounds have been undertaken during the past thirty years, mainly in America. Among the most prolific workers in this field are G. L. Keenan and W. M. D. Bryant. Keenan's studies have included sugars, amino acids, and substances listed in the U. S. Pharmacopoeia [5], while Bryant has studied derivatives of alcohols, aldehydes, and aliphatic acids [6], among many other compounds. It has been found with very

few exceptions that compounds in the same series can readily be distinguished from one another by determining their refractive indices or by other simple optical tests.

The optical method has played a valuable, and in some cases essential, part as a means of identifying the solid phases in phase-equilibrium studies. Thus, in investigations of high-temperature silicate systems, such as have been in progress for some years in America and at the Building Research Station in Britain, ordinary methods of thermal analysis are of little use, since equilibrium is attained so sluggishly. The method mainly adopted is to quench equilibrium mixtures of the components and examine the resulting solid under the polarizing microscope. Any liquid present in the original equilibrium mixture quenches to a glass, which can be recognized by its isotropic character. Crystalline solid phases are identified by their characteristic optical properties. In this way the thermal diagram may be built up. A knowledge of the equilibria in systems of this type is of fundamental importance in petrological research and in the study of cement, slags, and refractories. The classical example, which sheds much light on the constitution of Portland cement, is the system CaO–Al_2O_3–SiO_2 studied by Rankin and Wright [7], and in the same connection the important quaternary system CaO–$2CaO$, SiO_2–$5CaO$, $3Al_2O_3$–$4CaO$, Al_2O_3, Fe_2O_3 has been studied by Lea and Parker [8].

Optical methods play an important part in the study of refractories as such, and a good example is afforded by the changes undergone by silica bricks in the open-hearth furnace. In a soft-burned brick before use the silica is present mainly as quartz (figure 6(*c*)), distinguishable from the other polymorphic modifications of silica by its marked double refraction. During use the silica in the inner and hottest zone of the brick becomes converted to cristobalite (figure 6(*b*)), which is isotropic and thus immediately identifiable between crossed nicols. Adjoining this zone is a somewhat cooler one, where the silica has been converted to tridymite (figure 6(*c*)), which has a low double refraction, and also crystallizes in characteristic shapes. The widths of these zones show the temperature gradient to which the brick has been subjected, and this is an important factor in the life of the furnace lining.

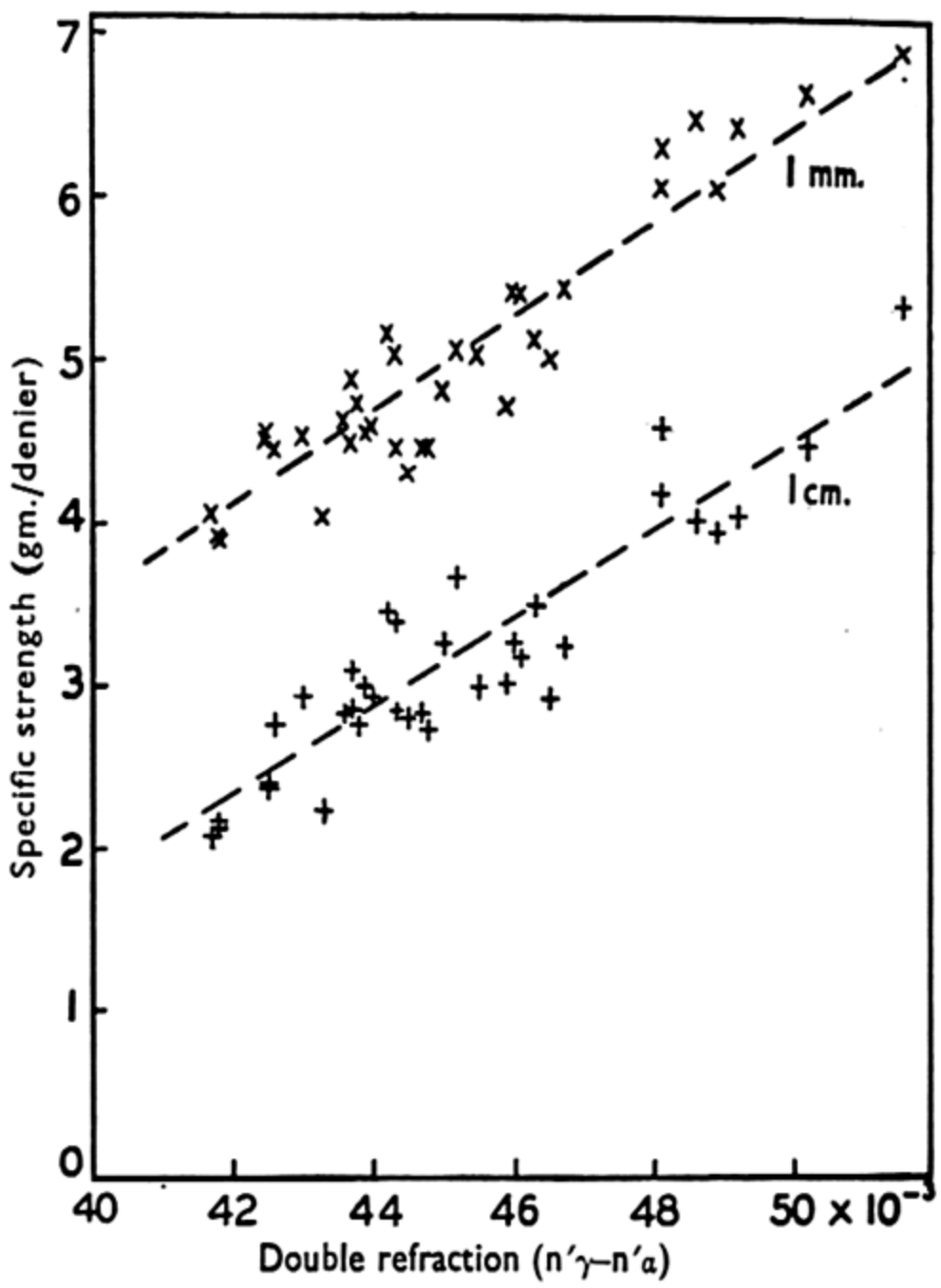


FIGURE 7 – *Relation between double refraction and strength of cotton fibres* (1 *mm. and* 1 *cm. lengths*).
(*n′γ and n′α are the indices for light vibrating respectively along and across the fibre.*)
(*Reproduced by permission of the British Cotton Industries Research Association.*)

Numerous investigations on the relation between the optical properties, and in particular the refractive indices, of fibres and their other physical properties have been undertaken. Thus it has been found by the British Cotton Industry Research Association [9] that there is a high degree of correlation between the birefringence of cotton fibres and their strength (see figure 7).

REFERENCES

[1] BUNN, C. W. *Chemical Crystallography* (Oxford, 1945). CHAMOT, E. M., and MASON, C. W. *A Handbook of Chemical Microscopy, Vol. I* (Wiley, 1938). HARTSHORNE, N. H., and STUART, A. *Crystals and the Polarizing Microscope* (Arnold, 1934).

[2] HARTSHORNE, N. H. *J. Soc. Chem. Ind.*, 1933, **52**, 367.

[3] BENEDICT, H. C. *J. Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 91.

[4] BELL, E. V., BENNETT, G. M., and MANN, F. G. *J. Chem. Soc.*, 1929, 1462.

[5] KEENAN, G. L. *J. Assoc. Off. Agr. Chem.*, 1944, **27**, 153.

[6] BRYANT, W. M. D., and MITCHELL, Jun. *J. Amer. Chem. Soc.*, 1938, **60**, 2748.

[7] RANKIN, G. A., and WRIGHT, F. E. *Amer. J. Sci.*, 1915, (4), **39**, 1.

[8] LEA, F. M., and PARKER, T. W. *Phil. Trans. Roy. Soc.*, 1934, **234**, No. 231, 1.

[9] MEREDITH, R. *Shirley Institute Memoirs*, 1944–5, **xix**, No. XXIII.

The principles of chromatography

A. J. P. MARTIN

Chromatography is a method of chemical analysis founded on differential adsorption in a counter-current process. Although the basic procedure of the method was very firmly established by the Polish botanist Tswett more than thirty years ago, it is only during the past decade that chemists have recognized its great value and made effective use of it. Dr Martin here describes the principal features of the practical technique, and discusses some theoretical considerations of importance in the use of the method.

Chromatography has been so widely used in the last fifteen years that to give an adequate account of its achievements would be a problem as difficult as to give an account of the achievements of distillation. Since its first use in the form of capillary analysis by Schönbein (1861) and its later development by Tswett (1906), chromatography is already quite indispensable in many fields, and may be expected to become so in any field where the separation of very similar substances is required. Although chromatography has a remarkably wide field of application, the method rests on principles which can be described without reference to specific examples. In the following discussion my illustrations are confined largely to partition chromatography with which I have myself been associated, not because it is more important but because it is less familiar.

Chromatography is a counter-current, or column, process. It bears the same relationship to simple methods of separation by adsorption, in which the adsorbent is merely stirred with the solution, as distillation with a fractionating column does to simple distillation. The analogy with the fractionating column is indeed close. Just as distillation with a fractionating column is equivalent to thousands of separate distillations, so chromatography, with its ordered movement of liquid relative to the adsorbent with which it is continuously equilibrating, is equivalent to a repeated stirring up with adsorbent and filtering. In many cases this differential rate of movement permits the separation, with only infinitesimal contamination, of substances whose adsorption is so similar that no useful separation could be obtained by simply stirring with the adsorbent.

The ideal chromatogram consists of a tube containing a column of porous adsorbent through which the solution is percolating. The proportion of liquid to solid at all points is constant, and the flow of liquid is uniform. Suppose now that a solution of some suitable solute runs into the column in place of the pure solvent. If in any thin cross-section of the column the fraction of the solute in the solvent is α, then $(1-\alpha)$ is adsorbed on the solid. Equilibrium between solid and liquid is, in this ideal case, instantaneous, and no diffusion occurs. It is obvious, since a fraction α is moving with the speed of the liquid and a fraction $(1-\alpha)$ is stationary, that the net rate of movement of the solute is α times the rate of movement of the liquid. *This ratio of the rate of movement of the solute to the rate of movement of the solvent* is called the R_F value. This ideal case is shown in figure 1; it has been interpreted by Wilson [1].

In fact, of course, equilibrium is not attained instantaneously. The solute has to move from liquid to solid and *vice versa*, and this has important practical consequences. For rapid equilibrium the distance over which diffusion must carry the solute must be made as small as possible. It is therefore nearly always a mistake not to use a finely ground adsorbent. Figure 2 shows how the band of solute loses its sharp edges when attainment of equilibrium is not instantaneous. The band approximates more and more closely to the 'error curve' shape as it progresses down the column [2].

So far it has been assumed that the ratio of the concentration of solute in the liquid and in the adsorbent at equilibrium is a constant, i.e. a linear adsorption isotherm has been assumed. This is usually not the case. Generally the proportion of solute in the liquid phase rises as the concentration is increased (Freundlich or Langmuir adsorption isotherm). Figures 3 and 4 show the resulting shapes of the bands. The R_F value rises with the concentration; consequently the front of the band moves faster than the back, and the band broadens. The front stays relatively sharp (figure 4), since the layer of diminishing

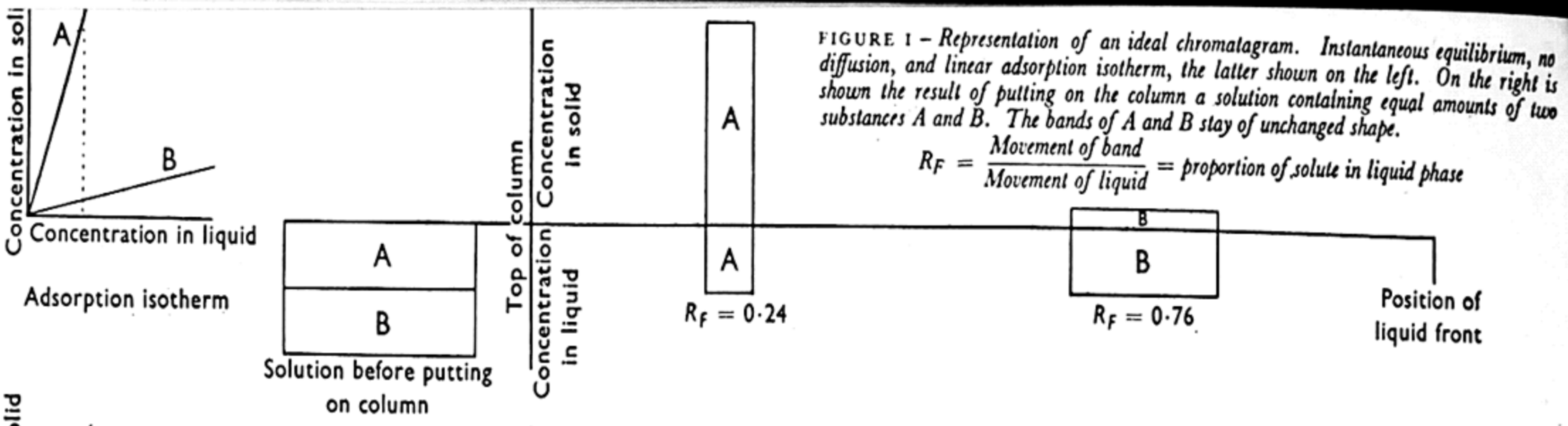


FIGURE 1 – *Representation of an ideal chromatagram. Instantaneous equilibrium, no diffusion, and linear adsorption isotherm, the latter shown on the left. On the right is shown the result of putting on the column a solution containing equal amounts of two substances A and B. The bands of A and B stay of unchanged shape.*

$$R_F = \frac{\text{Movement of band}}{\text{Movement of liquid}} = \text{proportion of solute in liquid phase}$$

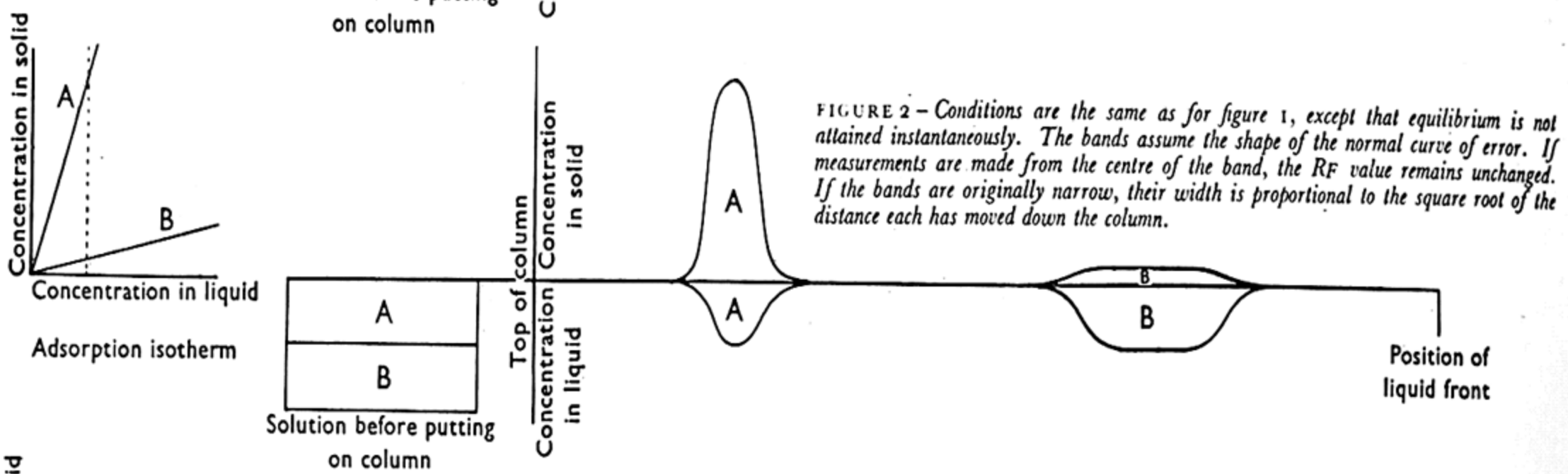


FIGURE 2 – *Conditions are the same as for figure 1, except that equilibrium is not attained instantaneously. The bands assume the shape of the normal curve of error. If measurements are made from the centre of the band, the R_F value remains unchanged. If the bands are originally narrow, their width is proportional to the square root of the distance each has moved down the column.*

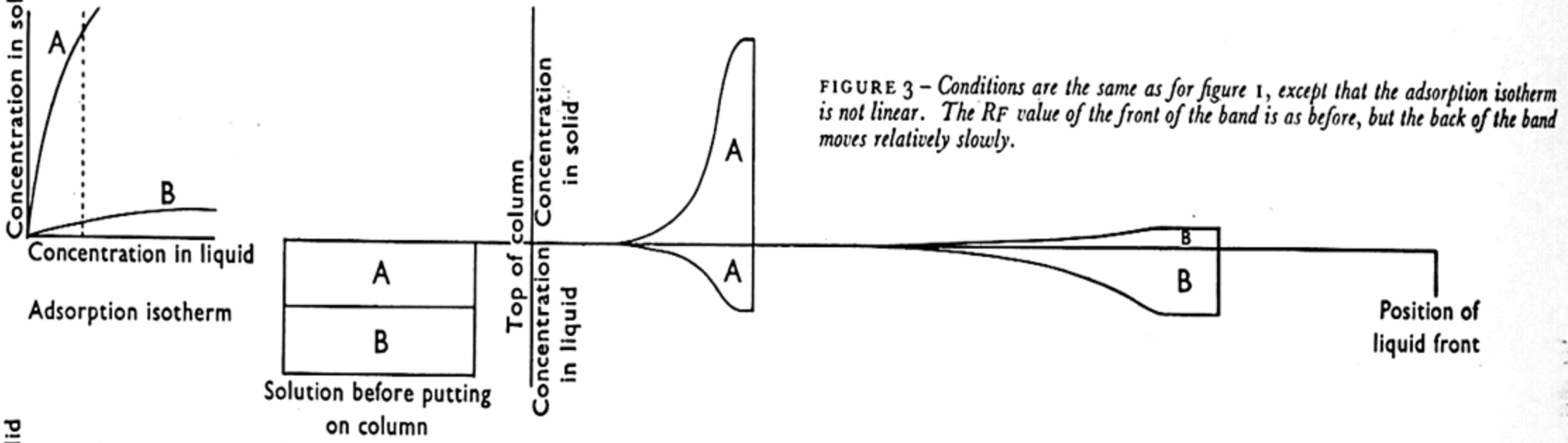


FIGURE 3 – *Conditions are the same as for figure 1, except that the adsorption isotherm is not linear. The R_F value of the front of the band is as before, but the back of the band moves relatively slowly.*

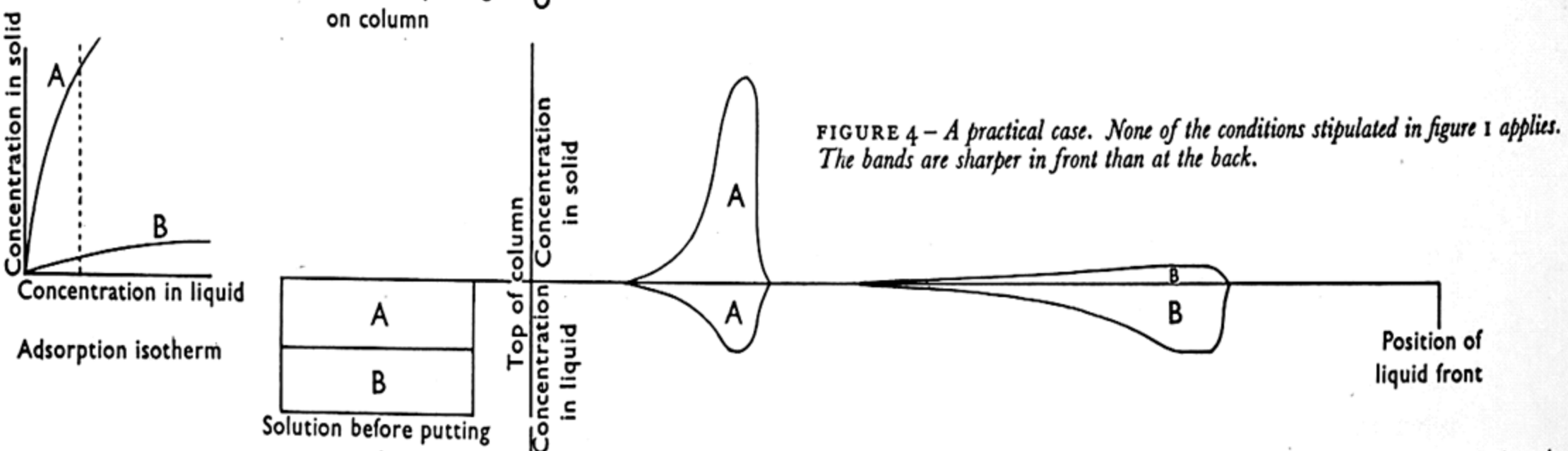


FIGURE 4 – *A practical case. None of the conditions stipulated in figure 1 applies. The bands are sharper in front than at the back.*

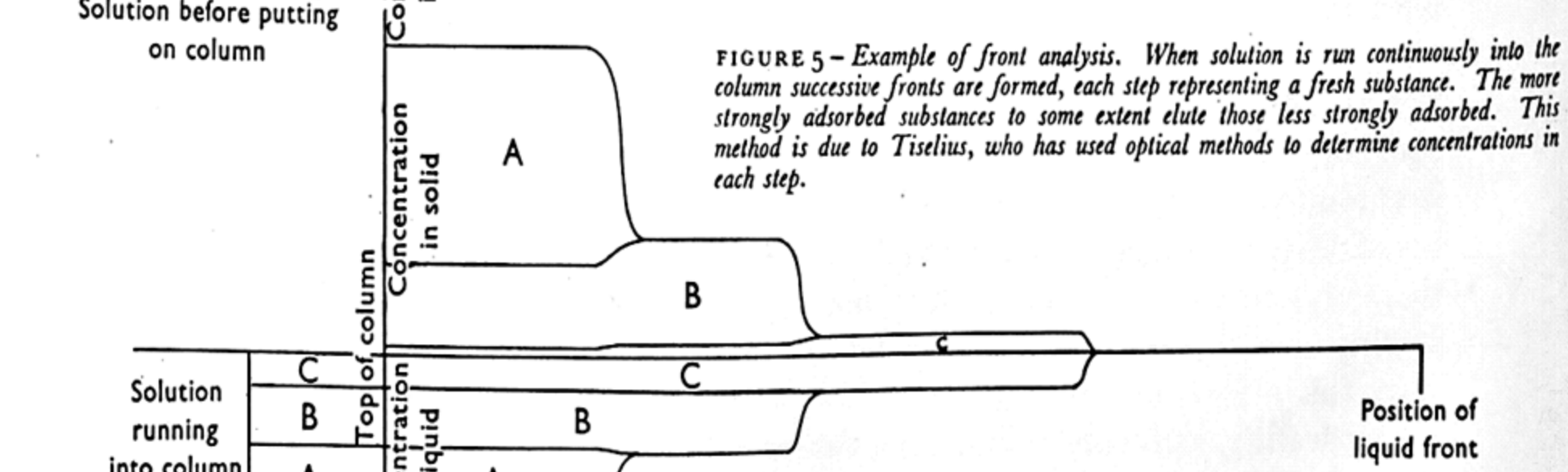


FIGURE 5 – *Example of front analysis. When solution is run continuously into the column successive fronts are formed, each step representing a fresh substance. The more strongly adsorbed substances to some extent elute those less strongly adsorbed. This method is due to Tiselius, who has used optical methods to determine concentrations in each step.*

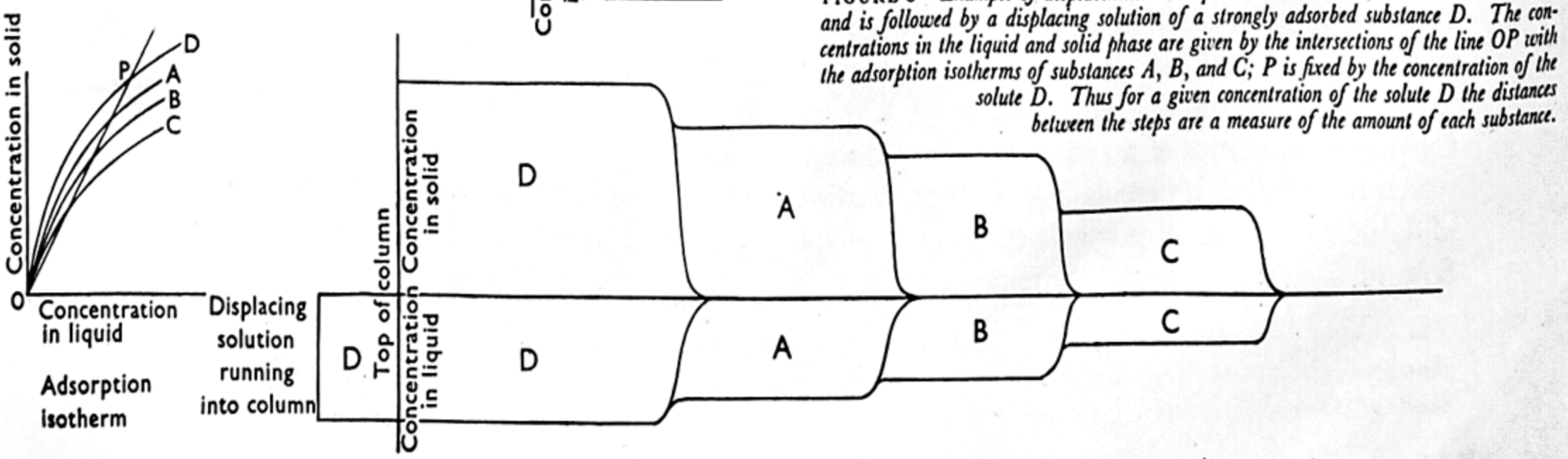


FIGURE 6 – *Example of displacement development. The solution is run into the column and is followed by a displacing solution of a strongly adsorbed substance D. The concentrations in the liquid and solid phase are given by the intersections of the line OP with the adsorption isotherms of substances A, B, and C; P is fixed by the concentration of the solute D. Thus for a given concentration of the solute D the distances between the steps are a measure of the amount of each substance.*

FIGURES 1–6 – *Typical examples of chromatographic adsorption. For further explanation see text.*

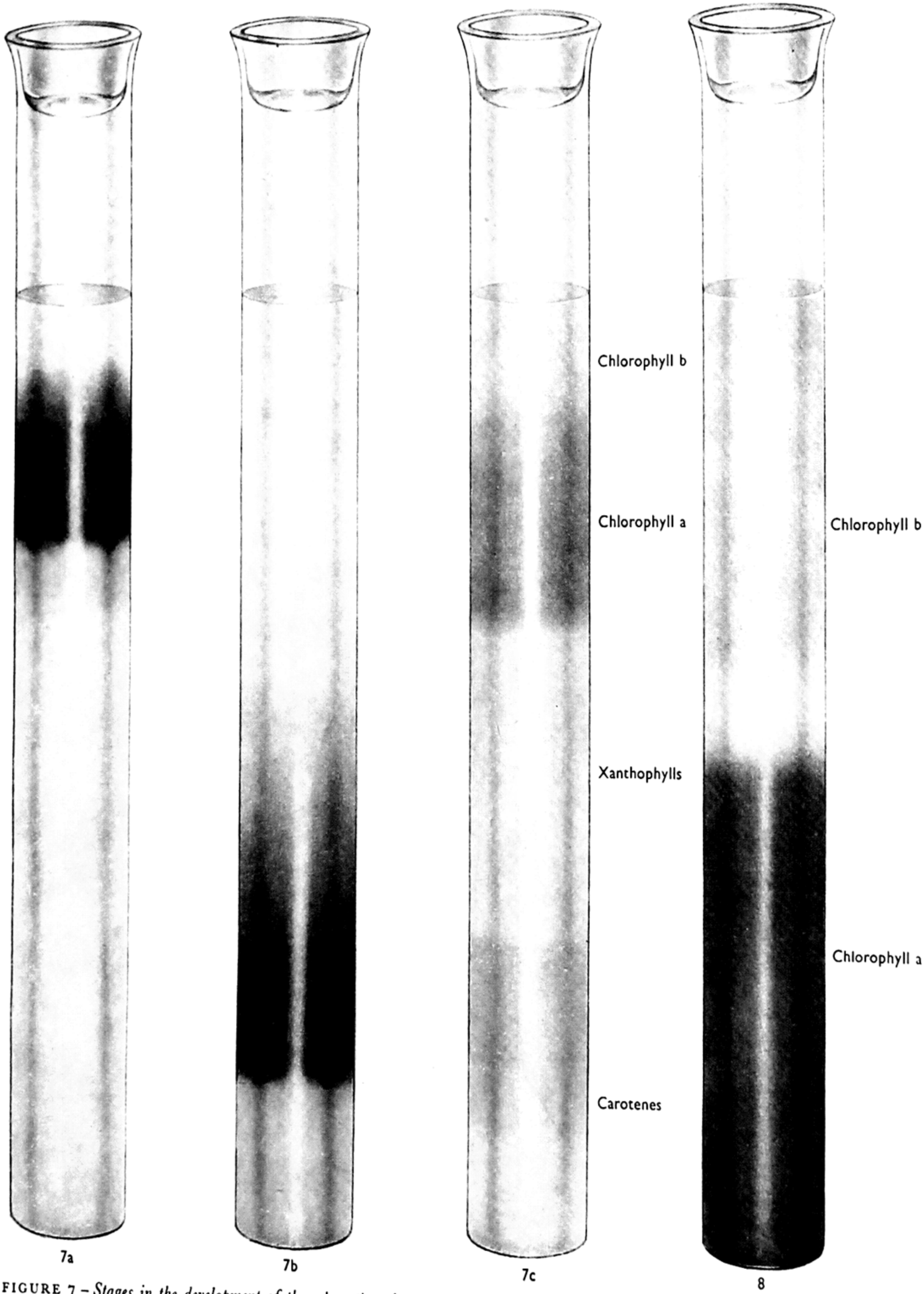


FIGURE 7 – *Stages in the development of the adsorption chromatogram formed when an extract of grass in cyclohexane is passed through a column of starch.*

(*a*) *Start of development. Colourless substances are displacing chlorophyll and carotene.* $R_F = 1$, *so no resolution can be seen.*

(*b*) *Most of the colourless material has been adsorbed, and the carotene band is showing in front of the chlorophyll.* $R_F < 1$.

(*c*) *The coloured bands have been separated, the pigments extracted again into cyclohexane, and the resulting solution passed through a new column. Displacing substances have been left on the old column. Elution development* (page 27) *shows bands of chlorophylls, xanthophylls, and carotenes.*

FIGURE 8 – *The same as* 7(*c*), *except that for development cyclohexane has been replaced by benzene.*

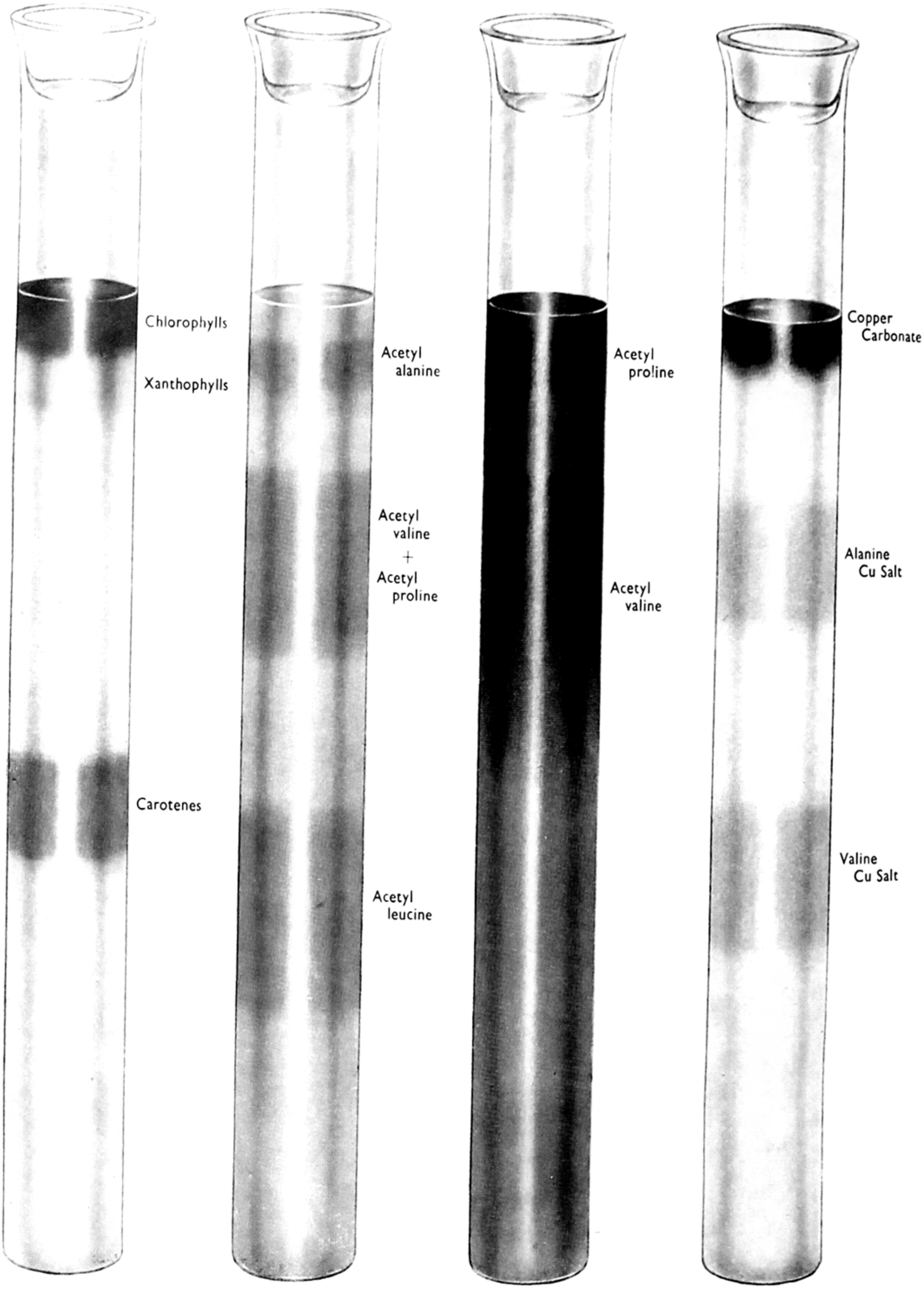


FIGURE 9 – *The same solution as that used for producing the chromatograms shown in figure 7 passed through a column of magnesium oxide. Chlorophylls are strongly retained. Elution development has revealed bands of xanthophylls and carotenes.*

FIGURE 10 – *Partition chromatogram showing separation of acetyl alanine, acetyl valine, acetyl proline, and acetyl leucine on a silica gel column. The silica gel was prepared with water containing methyl orange as indicator, and the position of the acetyl amino acids is shown by the red colour. The solvent is chloroform containing 1% of butanol.*

FIGURE 11 – *Separation of acetyl proline and acetyl valine on a column of silica gel, using a special indicator. The solvent is cyclohexane. Using columns of the type shown in figures 10 and 11, it is possible to estimate quantitatively the amount of alanine, leucine and isoleucine, phenyl alanine, tyrosine, and methionine contained in the hydrolysate of 20 mg. of protein.*

FIGURE 12 – *Separation of the copper salts of alanine and valine on a column of silica gel. The partition chromatogram has been developed with a mixture of chloroform and butanol.*

filter paper. The strip is hung from a glass trough in an atmosphere saturated with water and solvent. Solvent, also saturated with water, siphons over and down the strip. After 4–48 hours the strip is dried, sprayed with a solution of ninhydrin, and heated. The reagent reveals the position of the amino acids as coloured patches.

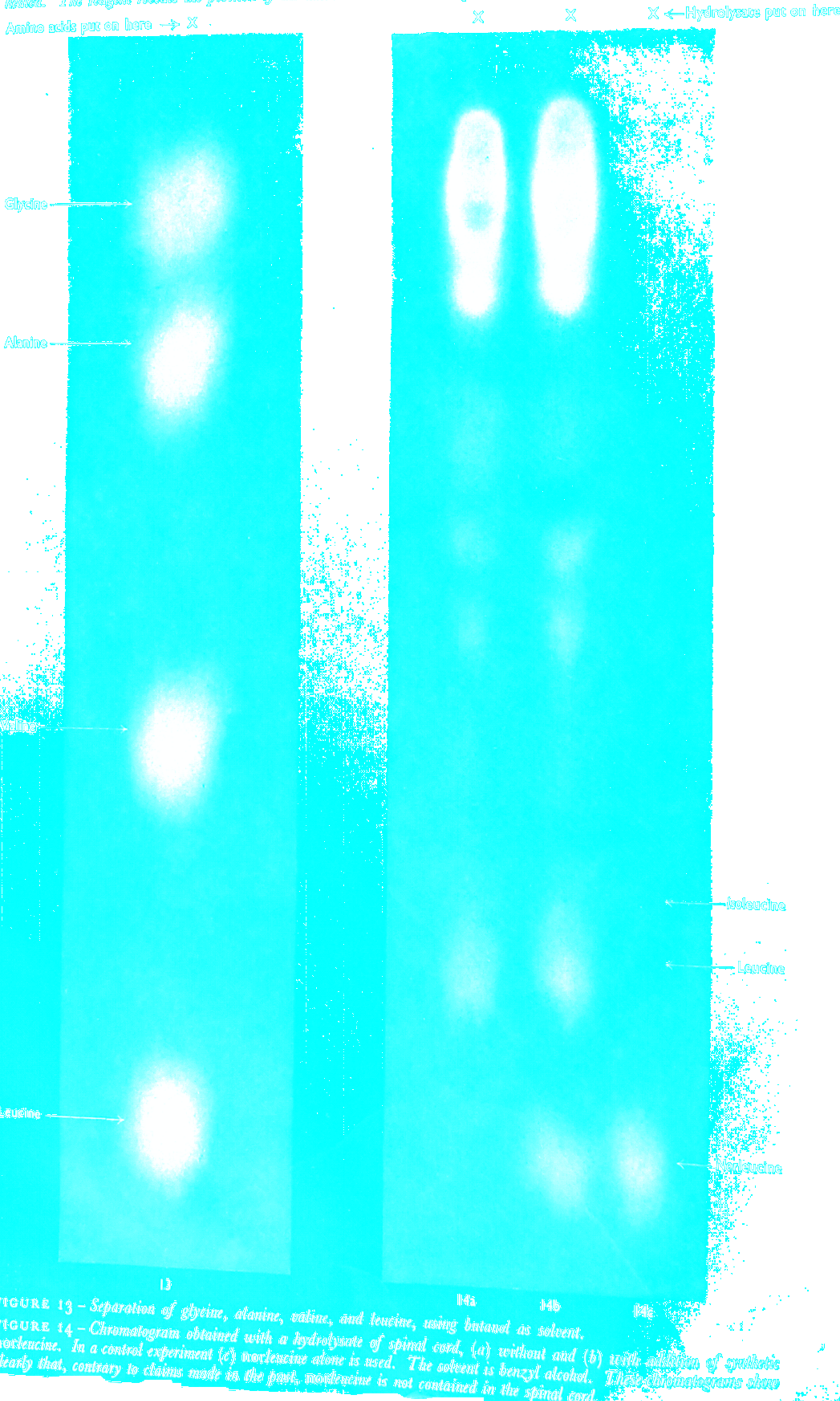


FIGURE 13 – *Separation of glycine, alanine, valine, and leucine, using butanol as solvent.*

FIGURE 14 – *Chromatogram obtained with a hydrolysate of spinal cord, (a) without and (b) with addition of synthetic norleucine. In a control experiment (c) norleucine alone is used. The solvent is benzyl alcohol. These chromatograms show clearly that, contrary to claims made in the past, norleucine is not contained in the spinal cord.*

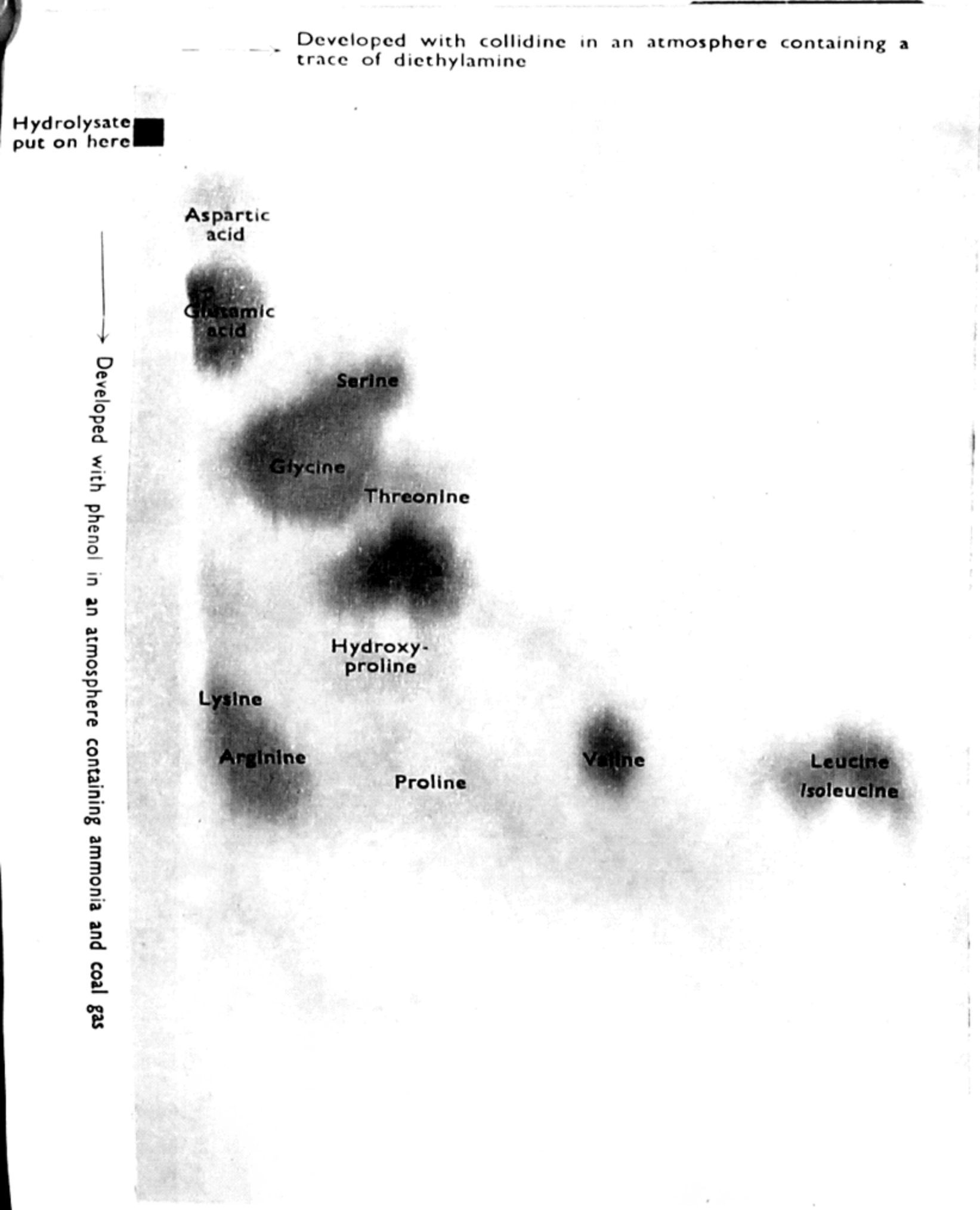


FIGURE 15 – *Two-dimensional chromatogram of gelatin on filter paper. A drop of the hydrolysate is placed near the corner of the sheet of paper. This is hung from the long side and the chromatogram developed with s-collidine. The paper is dried, hung from the short side, and the chromatogram developed with phenol. It is dried again, sprayed with ninhydrin, and heated. 300 mg. of gelatin were used for this experiment. As little as 1–2 mg. of most amino acids can be seen clearly on a two-dimensional chromatogram of this kind.*

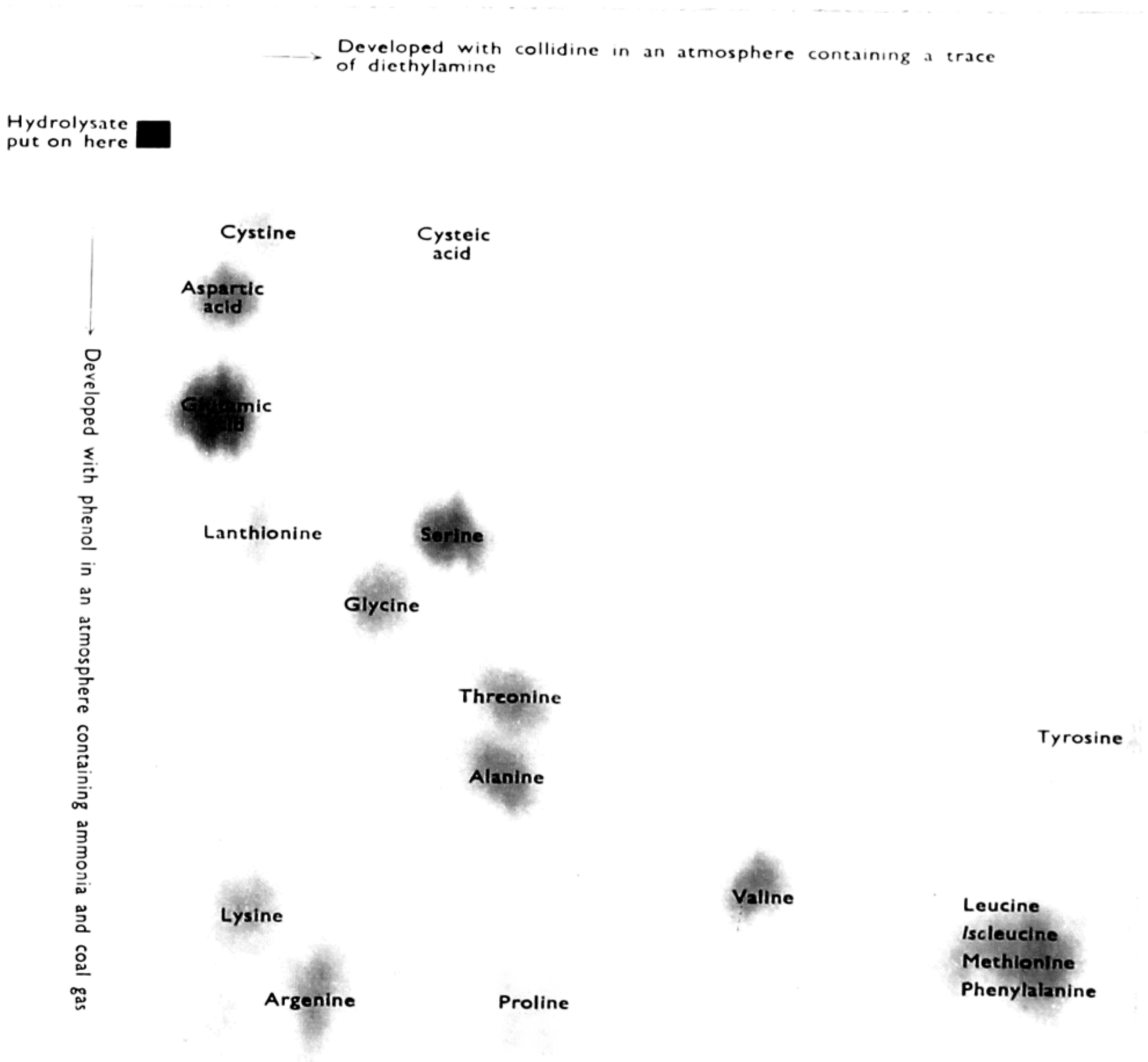


FIGURE 16 – *Two-dimensional chromatogram of tips of wool fibres. Procedure as for figure 15. Exposure to weather and light has converted some cystine to cysteic acid and some to lanthionine. Otherwise the picture resembles that of pure wool. The clump of unresolved amino acids in the right-hand bottom corner can be separated if benzyl alcohol and butanol are used in place of collidine and phenol, but then the other acids are crowded together.*

concentration at the front of the band, caused by diffusion and slow attainment of equilibrium, is continuously overrun by the faster-moving, more concentrated zone behind. The case illustrated in figure 3 has been interpreted by De Vault [3] and Weiss [4].

There is, however, a further complication. The adsorption of one substance may greatly modify the adsorption of another. This is particularly the case when the adsorption isotherms are of the Freundlich or Langmuir type. Figure 5 shows the result of running a relatively large volume of a solution of three substances down a column without 'developing' the chromatogram, i.e. further separating the bands, with pure solvent. If the adsorption of one were not influenced by another, the concentration in the steps would be the same as in the original solution.

If a mixed solution running into the column, as in figure 5, is replaced by a solution of another and more strongly adsorbed substance (*D*), the state shown in figure 6 soon occurs, since each substance 'elutes' or washes off the substance in front of it. In the absence of interaction, elution development would be superposed on a background of *D*. This is interesting as representing a steady state, the bands of *A*, *B*, and *C* moving down the column with unchanging shape.

METHODS OF CHROMATOGRAPHY

Figures 4, 5, and 6 represent three different ways in which chromatograms can be employed. The method of figure 4 (elution development) is the most familiar in the laboratory. After adequate development the column is cut up and the adsorbent extracted with a suitable eluting solvent, or development is continued until the bands run separately from the bottom of the column in the solvent. The latter method of working has been misleadingly named 'liquid chromatography.' In using this method a linear adsorption isotherm is desirable, as otherwise each band tends to tail more or less into the succeeding band.

The method of figure 5, often not recognized as chromatography at all, is extremely widely used in industry for water softening, recovery of valuable ions in industrial wastes, and for solvent recovery from air or other gases. It is remarkable that this solvent recovery process seems to be the only use at present of gas as the mobile fluid in chromatography, though there appears to be no reason why it should not be a valuable method for analytical purposes. Recently Tiselius has applied this method to analysis. He has developed 'front analysis,' as he calls it, into a most powerful tool for dealing with intractable mixtures such as amino acids and peptides. By applying the optical techniques developed for electrophoresis and ultracentrifugal investigations to the liquids issuing from a chromatogram, a peak is obtained wherever the concentration changes. Thus figure 5 would show three peaks.

Tiselius has also developed the 'displacement development' method (figure 6), recording the concentration of the effluent from the column with an automatic interferometer. A record is obtained of a series of steps, the length of each of which is a measure of the amount of each substance present, while the height is determined by the adsorption isotherm.

In distinction to the elution development method, a non-linear adsorption isotherm is an advantage with the last two methods, since the fronts remain sharper and are easier to observe.

ADSORBENTS AND SOLVENTS USED

Alumina and Other Metallic Oxides. The choice of adsorbent and solvent has hitherto been almost entirely empirical. The adsorbent most commonly used in laboratory work is alumina, with non-polar solvents such as petrol. Various metallic oxides and salts behave more or less similarly. The method of preparation of the adsorbent is as important as its chemical composition. Polar and polarizable groups in the solute are the chief determinants of adsorption behaviour with this class of adsorbent. Similarly, elution is caused by polar or polarizable solvents. If a solvent forms hydrogen bonds, it is usually a good eluting agent. These adsorbents differ widely in strength but little in selectivity; the order of bands of different substances is seldom different on different adsorbents of this class.

Carbon. Active carbon, though long used as an adsorbent for decolorizing solutions and for solvent recovery, has only recently been used in analytical chromatography. The adsorption isotherms on carbon are usually far from linear, and it is thus most suitable for 'front analysis' and 'displacement development' (see above). It seems to have several or perhaps many different kinds of adsorbing sites, and carbons with widely different adsorptive selectivity can be produced by different methods of activation. In general it may be said that fatty chains, and particularly aromatic rings, determine adsorption on carbon, while polar groupings are less important. Thus adsorption of amino acids, for example, takes

place from aqueous solution, and they can be eluted by phenol or ephedrine. Pre-treatment of the carbon is usually necessary to prevent irreversible adsorption and catalytic oxidation.

Ion Exchangers. Ion-exchange materials have long been used for water softening but have only recently been used to any great extent in analytical chromatography. They are essentially large insoluble acids or bases which form insoluble salts. The first of such substances to be employed, the zeolites, were unstable in acid solution, and were used to exchange Na^+ for other cations. Adams and Holmes showed that certain synthetic resins possess exchange properties. Sulphonated coal or resins containing sulphonic acid groups are now in use, and will exchange H^+ ions for other ions. There are similarly basic resins which will exchange anions. With these adsorbents the adsorbed molecules are held by electrostatic forces, and it is charge, not molecular structure, that chiefly determines adsorption. Elution is effected by acid, alkaline, or salt solutions.

PARTITION CHROMATOGRAMS

Martin and Synge [2] have introduced silica gel into chromatographic analysis. Dry precipitated silica will take up about half its weight of water without appearing to become wet. A chromatogram can be made with such saturated silica and any solvent not completely miscible with water. With a suitable choice of solvent no adsorption occurs on the silica itself, and the formation of the chromatogram depends entirely upon partition between solvent and water. A typical column is illustrated in figure 10. In such a partition chromatogram the calculated R_F value, derived from the partition coefficient and amounts of water and immiscible solvent, agrees with the observed value.

Other liquids may be used in place of water, and starch, cellulose, or other substances in place of silica. Cellulose in the form of filter paper is a particularly useful material. Using narrow strips of paper it is possible to produce chromatograms analogous to those produced when ordinary columns of material are used. The use of paper strips is illustrated in figures 13 and 14. By using squares of paper (figures 15 and 16) a twofold separation can be effected. The solution to be analysed is applied at one corner of the square and a chromatogram is formed in the same way as when a strip of paper is used. To avoid evaporation the paper must be placed in an enclosure the atmosphere of which is saturated with respect to the solvents used. The paper is then dried, turned through 90 degrees, and the process repeated. A new solvent is used and each 'band' of the initial chromatogram is made the starting-point of another 'strip' chromatogram. The final result is to spread the constituents of the mixture over the whole sheet of paper instead of confining them to the original strip.

The partition chromatogram is highly selective, since solvents may be chosen which associate with particular groupings in the solute. A close analogy can be drawn between the effect of association on the partition coefficient between two liquids and between liquid and vapour. In the latter case association may give rise to azeotropic mixtures.

REFERENCES

[1] Wilson. *J. Amer. Chem. Soc.*, 1946, **62**, 1583.
[2] Martin and Synge. *Biochem. J.*, 1941, **35**, 1358.
[3] De Vault. *J. Amer. Chem. Soc.*, 1943, **65**, 532.
[4] Weiss. *J. Chem. Soc.*, 1943, 297.

The Chemical Society of London

After a delay of six years occasioned by the war, the Chemical Society (of London) will celebrate the centenary of its foundation on 15th, 16th, and 17th July, 1947. Outstanding among the several important events which will mark the occasion will be the delivery of the Faraday Lecture by Sir Robert Robinson, a past President of the Chemical Society and now President of the Royal Society. The centenary celebrations will be followed by the Eleventh International Congress of Pure and Applied Chemistry, also to be held in London. Many distinguished overseas delegates have been invited to attend, and if all are able to do so there will be seen in London next July perhaps the greatest international gathering of chemists ever to have taken place.

Organosilicon compounds and their industrial development

D. V. N. HARDY

Organosilicon compounds have been investigated for over eighty years, an outstanding contribution having been made by Professor F. S. Kipping, F.R.S., but it was only towards the end of the recent war that mention began to be made of commercial developments. Owing largely to difficulties in obtaining the new materials, first-hand information has hitherto been very scanty, and the precise nature and importance of the substances have been obscured by a secrecy necessitated by both military and commercial considerations.

Although initially studied by a sequence of investigators on the Continent, notably Friedel and his students Crafts and Ladenburg, the chemistry of organosilicon compounds will always be associated with Professor F. S. Kipping and his school of research workers at University College, Nottingham. Starting in 1899, Kipping diligently pursued the subject for close on forty years, and contributed over fifty papers to the *Journal of the Chemical Society*. The work was arduous and beset with experimental difficulty, not the least being a remarkable tendency of the compounds to form amorphous, glue-like products, but with great patience Kipping went on to collect an invaluable mass of precise and detailed information, the accuracy of which has occasionally been challenged but always upheld.

Academic study of organosilicon compounds progressed along classical lines. It consisted chiefly in the preparation and characterization of the various compounds and in the determination of their chemical properties, with theoretical interest focused mainly upon the degree of similarity between organosilicon compounds and their carbon analogues. This similarity proved to be slight. In its ability to combine with itself and with other elements, silicon cannot approach the versatility of carbon, and the facile, subtle variety of organic reactions is not encountered in organosilicon chemistry. Of paramount importance among silicon compounds is the remarkable tendency to form large molecules containing chains, rings, or networks of alternating oxygen and silicon atoms. Silicic acid and the polysilicates are built on this plan, and so are many oxygenated organosilicon compounds.

The methods for preparing organosilicon compounds are few, and consist principally of treating a silicon halide or an alkyl silicate with an organometallic compound or its equivalent. Friedel and Crafts [1] used silicon tetrachloride and zinc alkyls:

$$SiCl_4 + 2Zn(C_2H_5)_2 \longrightarrow Si(C_2H_5)_4 + 2ZnCl_2$$

and Ladenburg [2] showed not only that ethyl orthosilicate may be employed in place of silicon tetrachloride but that arylchlorosilanes can be prepared with mercury diaryls:

$$2SiCl_4 + Hg(C_6H_5)_2 \longrightarrow 2C_6H_5SiCl_3 + HgCl_2$$

Arylsilanes are also accessible by the interaction of silicon tetrachloride, an aryl halide, and sodium [3]:

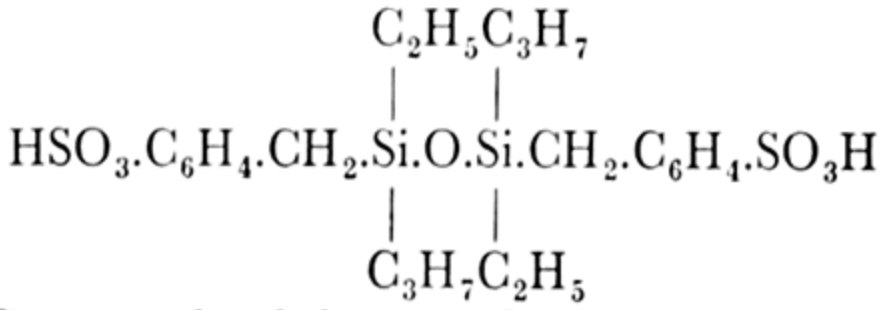
$$4C_6H_5Cl + SiCl_4 + 8\,Na \longrightarrow (C_6H_5)_4Si + 8NaCl$$

A valuable extension was made by Kipping, who introduced the use of Grignard reagents, with all their elegance and flexibility. All these synthetic methods permit the introduction of from one to four univalent organic radicals, either in one operation, by controlling the relative proportions of the reagents, or by successive treatment of the purified intermediate compounds with the same or different reagents:

$$SiCl_4 + CH_3MgBr \longrightarrow CH_3SiCl_3$$
$$CH_3SiCl_3 + C_2H_5MgBr \longrightarrow C_2H_5(CH_3)SiCl_2$$
$$C_2H_5(CH_3)SiCl_2 + C_3H_7MgBr \longrightarrow C_3H_7(C_2H_5)(CH_3)SiCl$$
$$C_3H_7(C_2H_5)(CH_3)SiCl_2 + C_6H_5MgBr \longrightarrow C_3H_7(C_2H_5)Si(CH_3)C_6H_5$$

An immediate consequence is that reaction cannot be confined to a particular intermediate stage, so that not only may yields be poor but the products may be difficult to separate by fractional distillation. Kipping's initial objective was to determine whether silicon resembles carbon in having an equispatial distribution of the four valencies. By the method outlined above he prepared a number

of asymmetric compounds and their salts with optically active bases, but was unable to resolve any compound containing a single silicon atom. He was, however, successful [4] in obtaining the optical antipodes of such compounds as 1, 2-dibenzyl-1, 2-diethyl-1, 2-dipropyldisiloxane-disulphonic acid[1]:



Compounds of the type R_3SiX (where R is a univalent hydrocarbon radical and X is a halogen atom or an alkoxyl group) readily hydrolyse to the corresponding silanols. These are usually high-boiling oils, or even crystalline solids, which may be readily dehydrated to disiloxanes. For example, triethylchlorosilane gives triethylsilanol (b.p. 184° C), which has an odour like camphor, and viscous hexaethyldisiloxane (b.p. 231° C):

$$(C_2H_5)_3SiCl + H_2O \longrightarrow (C_2H_5)_3SiOH$$
$$\longrightarrow (C_2H_5)_3Si.O.Si(C_2H_5)_3$$

Such structures do not admit a greater degree of complexity, but it is quite otherwise with the products obtained by hydrolysing compounds of type R_2SiX_2. By carrying out the hydrolysis under the mildest conditions it is possible to isolate the simple silandiols:

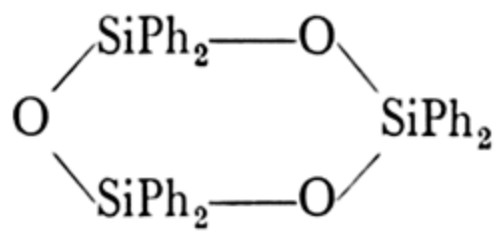
$$(C_2H_5)_2SiCl_2 + 2H_2O \longrightarrow (C_2H_5)_2Si(OH)_2$$

but these are very prone to undergo dehydration, and more complicated products usually arise, such as the syrup of high molecular weight obtained by Kipping and Martin [5] from diethyldichlorosilane. This syrup could be distilled without decomposition below 300° C, and possessed the empirical formula $C_4H_{10}SiO$. From diphenyldichlorosilane Kipping [6] was able to isolate the simple diphenylsilandiol, and both cyclic and linear condensation products of the following formulae:

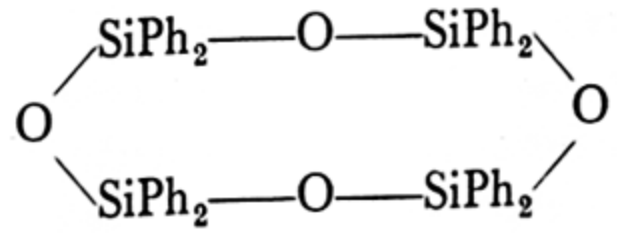
$HO.SiPh_2.O.SiPh_2.OH$
Tetraphenyldisiloxandiol (m.p. 113° C)

$HO.SiPh_2.O.SiPh_2.O.SiPh_2.OH$
Hexaphenyltrisiloxandiol (m.p. 112° C)

$HO.SiPh_2.O.SiPh_2.O.SiPh_2.O.SiPh_2.OH$
Octaphenyltetrasiloxandiol (m.p. 128·5° C)



Hexaphenylcyclotrisiloxane
(m.p. 188° C)

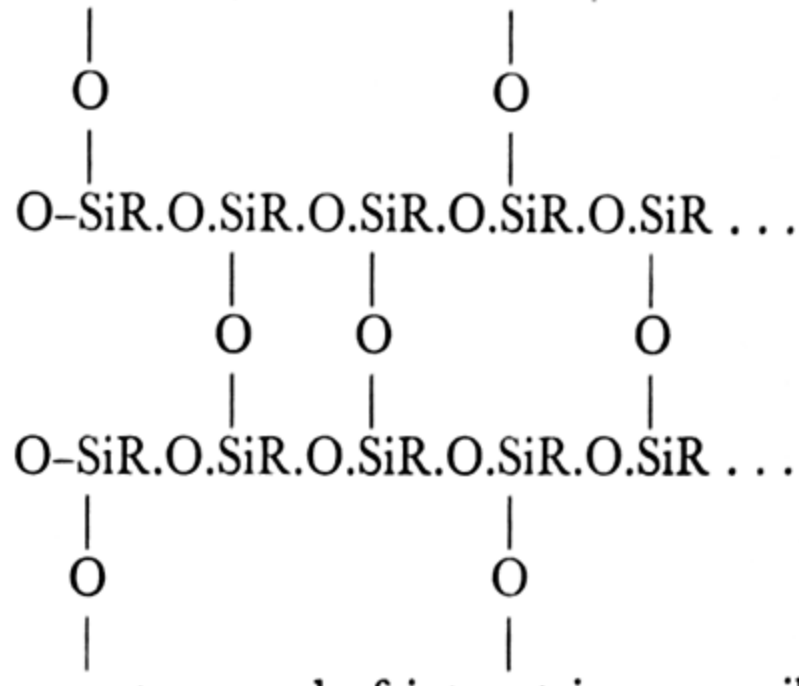


Octaphenylcyclotetrasiloxane
(m.p. 201° C)

Yet more complex compounds with longer chains and larger rings must account for the glue-like products into which the simpler compounds readily pass when heated. Intermediates of type $RSiX_3$ are hydrolysed to organosiloxanols:

$$R.SiX_3 + 2H_2O = R.SiO.OH + 3HX$$

These are usually amorphous powders or hard, brittle solids; many have no definite melting-point, and some are quite infusible. They consist of condensation products of varying degrees of complexity derived from the hypothetical organosilantriols ($RSi(OH)_3$), and may be of linear, cyclic, or cross-linked structure, the end-product of the dehydration process being cross-linked, insoluble, and infusible:



The great renewal of interest in organosilicon chemistry follows naturally from the intensive study and commercial development of high polymers. Here is a new class of highly condensed materials possessing a considerably greater degree of thermal stability than the accepted plastics. Their basic structure of recurrent siloxane units, analogous to that of the silicates, suggests that they may be good insulators of electricity. It would appear that this line of thought was being pursued by Russian investigators at an early stage, for in 1932 Dolgov [7] published a review of previous work on organosilicon compounds, and in 1935 Shtetter [9] patented the production of substituted chlorosilanes from silicon

[1] The system of nomenclature employed is that of R. O. Sauer [8].

tetrachloride and the simpler unsaturated hydrocarbons such as acetylene and ethylene. A few years later, several papers were published by Andrianov [10] and by Kotow [11] on the condensation products of the alkyl and arylsiloxanols (R.SiO.OH) and their application as heat-hardening resins. The products were too brittle for use alone, but when mixed with drying oils they gave satisfactory insulating varnishes.

In the United States, work on organosilicon compounds has been highly competitive. Initially there were three independent groups, represented by the Corning Glass Works, the Mellon Institute, and the General Electric Company, but at a later stage the first two and the Westinghouse Electric Corporation joined forces. Dr E. C. Sullivan, head of the Corning research department and discoverer of 'Pyrex' glass, desired a heat-resistant resin which could be used for impregnating glass fabric to give a flexible electrical insulation, and in 1931 Dr J. F. Hyde was assigned the task of making such a resin from organosilicon compounds. At the Mellon Institute, Dr G. R. McGregor went a long way towards an independent solution of the same problem before collaborating with Hyde. Other useful products were discovered, and it soon became necessary to begin manufacture. For this purpose the co-operation of the Dow Chemical Company was sought, and in 1943 the Dow-Corning Corporation was formed to manufacture and develop the new organosilicon products. These were dubbed 'silicones,' a term originally used by Kipping for the analogues of ketones. The Dow-Corning plant is based on the Grignard method of synthesis, and has a monthly output of 40–50 tons of various silicone products.

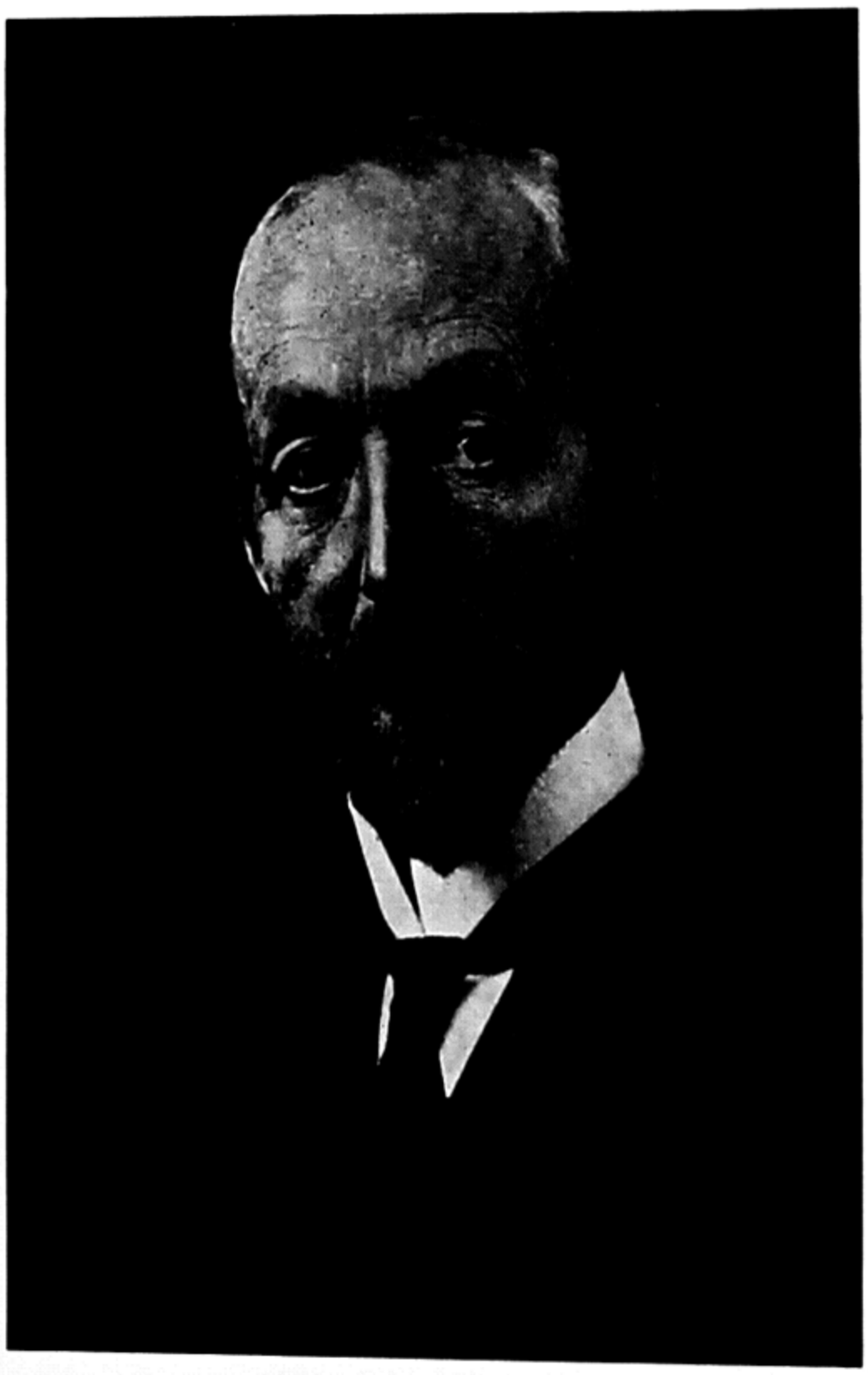


FIGURE 1 – *Professor F. S. Kipping, F.R.S.*

The research and development programme of the General Electric Company has been most energetically carried out by a large group of competent research workers, notably by Dr E. Rochow, and this powerful concern will shortly be in a position to manufacture a complete range of silicone products. So far, production has been on a pilot-plant basis with a monthly output of about two tons. Of major importance has been the discovery of a new method [12] for producing organosilicon intermediates. This consists in bringing the vapour of an alkyl or aryl halide into contact with an intimate mixture of silicon and copper or silver at an elevated temperature:

$$Si + 2CH_3Cl \xrightarrow{Cu} (CH_3)_2SiCl_2.$$

The catalytic action of copper and silver is thought to be connected with the transitory formation of their organocompounds [13]:

$$CH_3Cl + Cu \longrightarrow CH_3CuCl.$$

The process is particularly effective with methyl chloride at 280–300° C, and leads to a complex mixture of methylchlorosilanes, chief of which is dimethyldichlorosilane (b.p. 70° C). Methyltrichlorosilane (b.p. 66° C) is also present in notable proportion, while trimethylchlorosilane (b.p. 57° C) and methyldichlorosilane (b.p. 42° C) are minor constituents. In the preparation of certain silicone products it is necessary to employ highly purified intermediates so that the degree of cross-linkage may be kept under close control. Owing to the proximity of their boiling-points, the methylchlorosilanes can be separated only in highly efficient fractionating columns (80–100 theoretical plates). This new synthesis is well adapted to large-scale production, and it may be expected that manufacturing costs will be lower than with the Grignard process. Unfortunately the direct synthesis is not uniformly successful, so that wherever it proves impracticable or uneconomic the Grignard method will still hold sway.

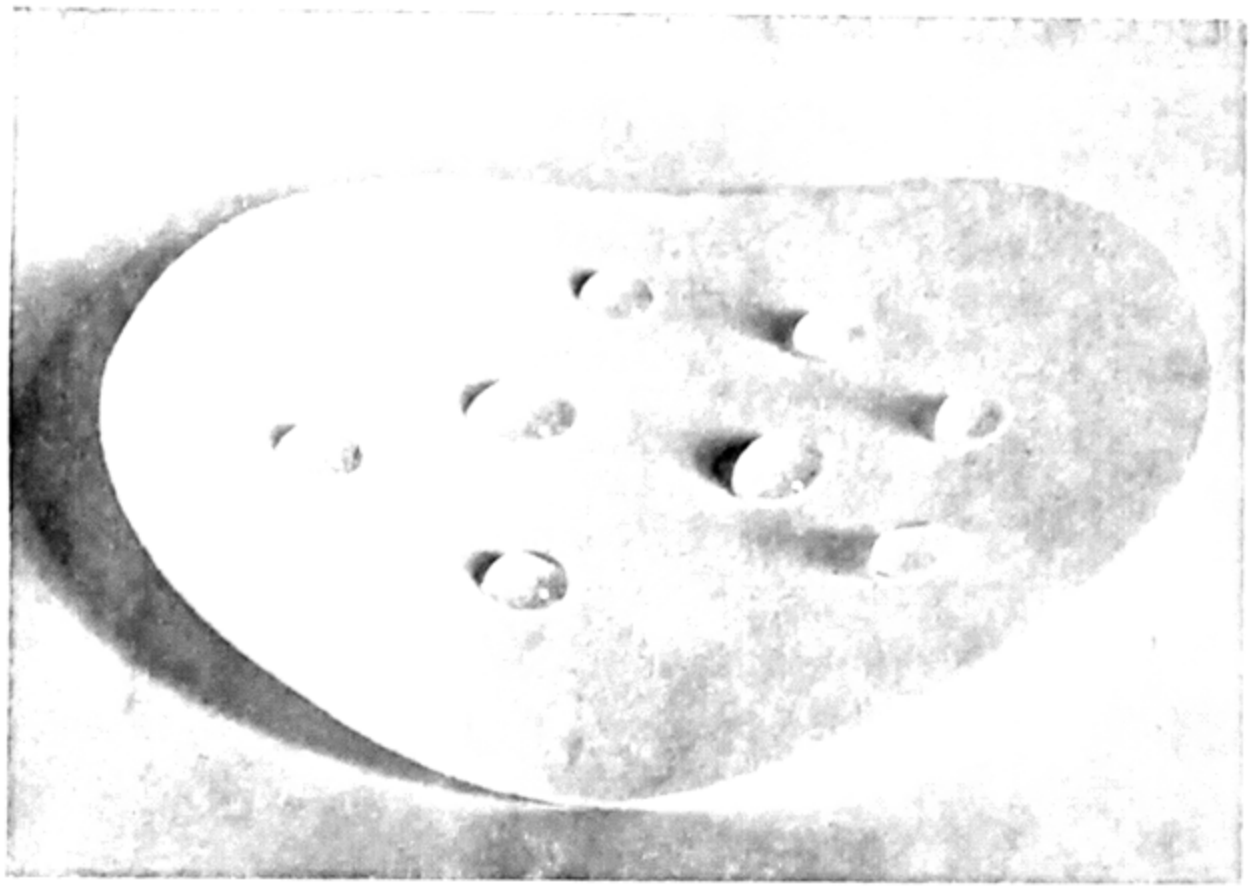


FIGURE 2 (*above*) – *Water-repellent filter paper. The filter paper was exposed for fifteen seconds to the vapour of methyltrichlorosilane and then to gaseous ammonia. The water drops are not absorbed and do not wet the paper, which retains its strength and permeability to gases and most other liquids.*

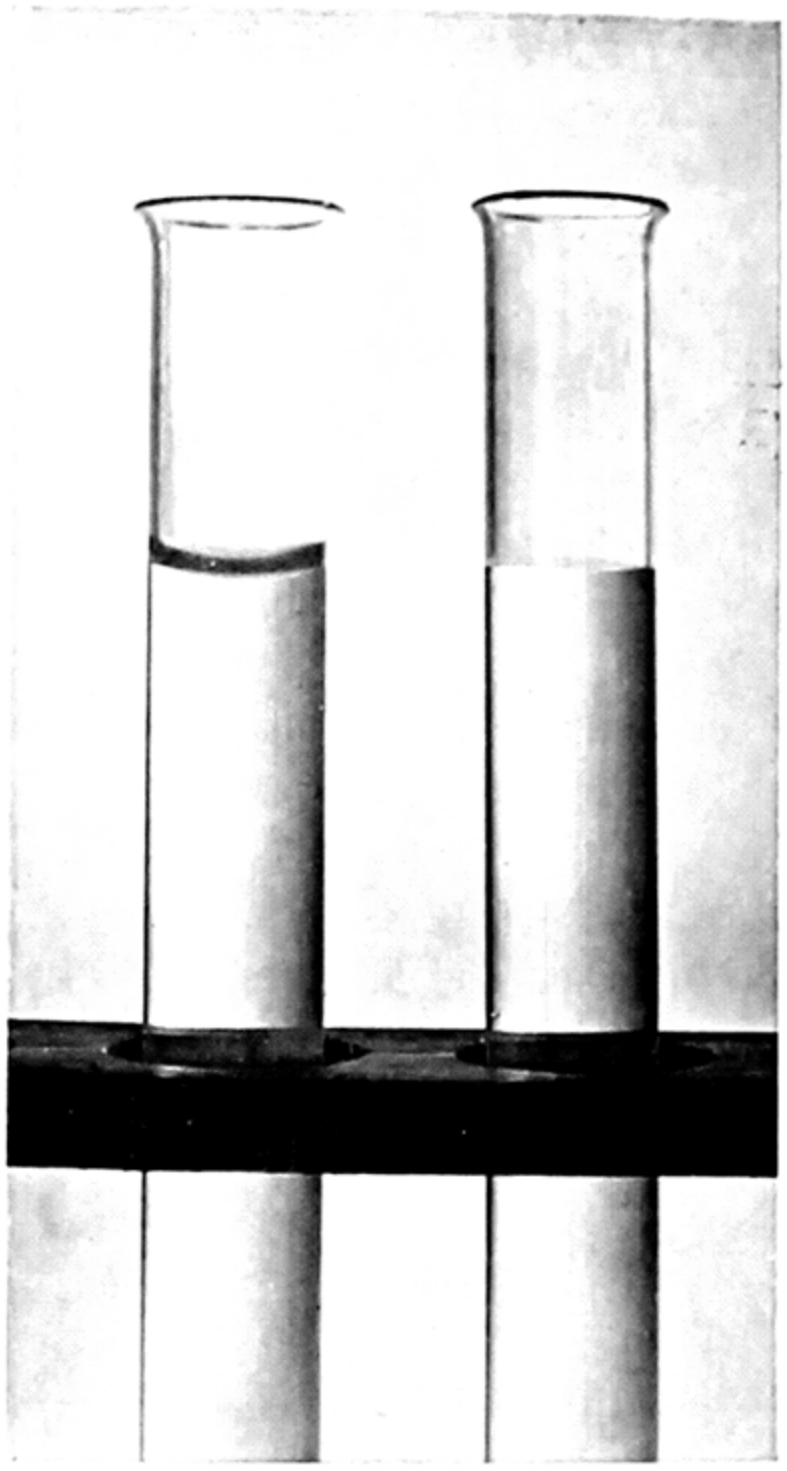


FIGURE 3 (*right*) – *Glass tubes containing water. On the left is a normal clean test tube, showing the meniscus, characteristic of a liquid which wets glass. The right-hand tube is a similar tube, the inside of which has been in brief contact with liquid dimethyldichlorosilane and then thoroughly cleansed with alcohol and ether. The water surface is flat because the glass is not wetted.*

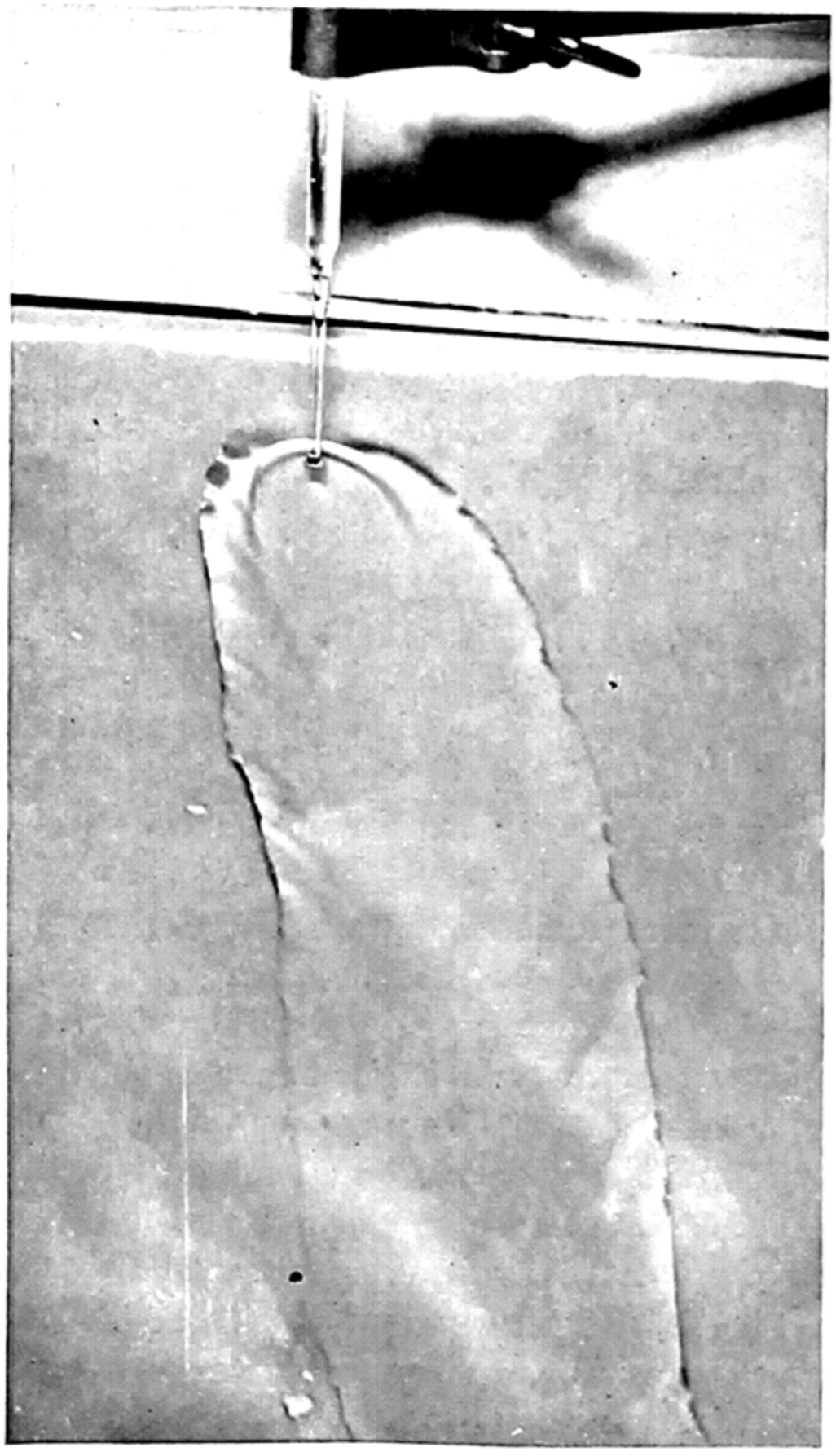


FIGURE 4*a* – *Water flowing down a clean glass plate inclined at 35°. The thin and wide spread shows that the glass is thoroughly wetted. The shape of the moving water film remains substantially unaltered.*

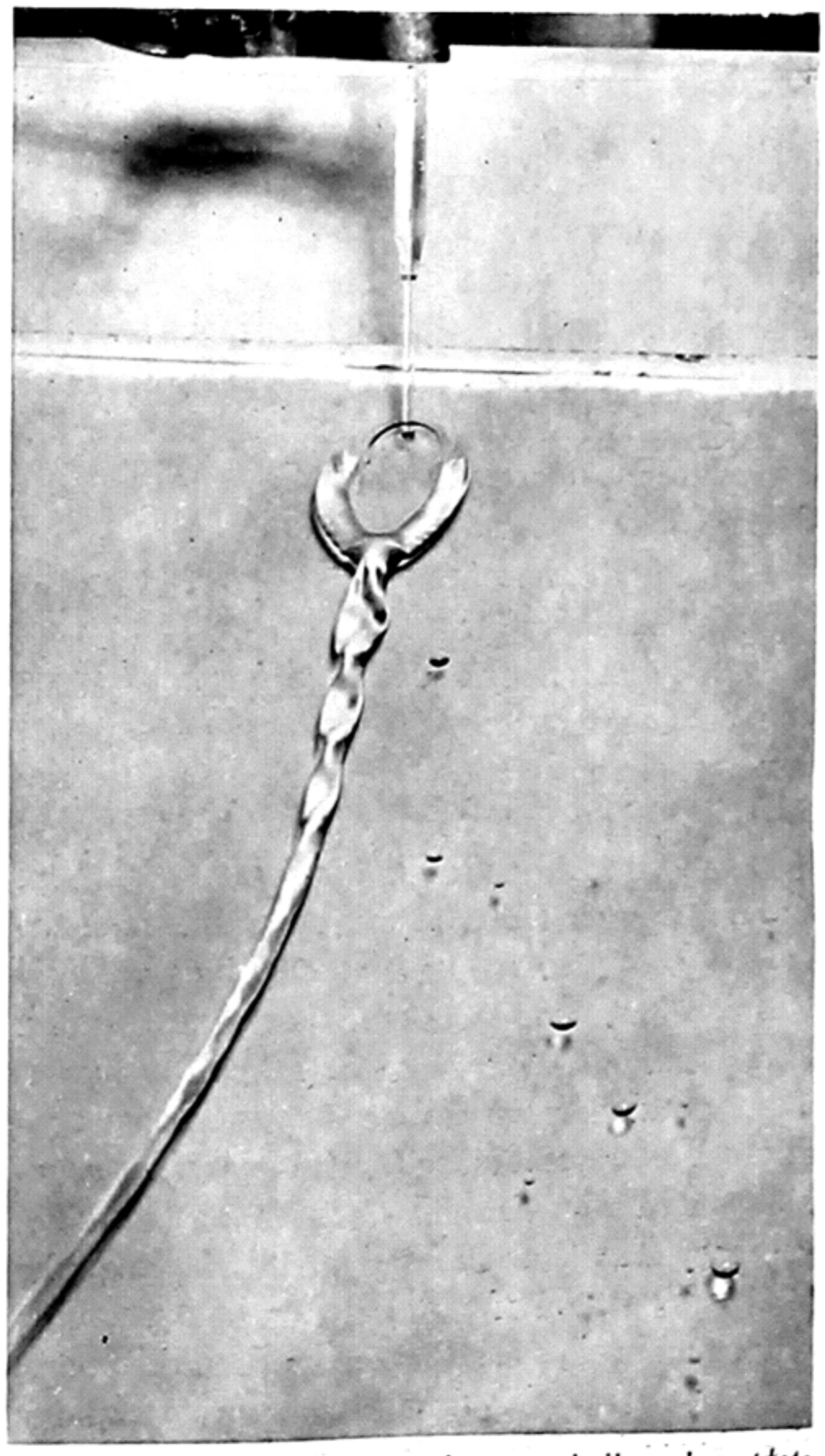


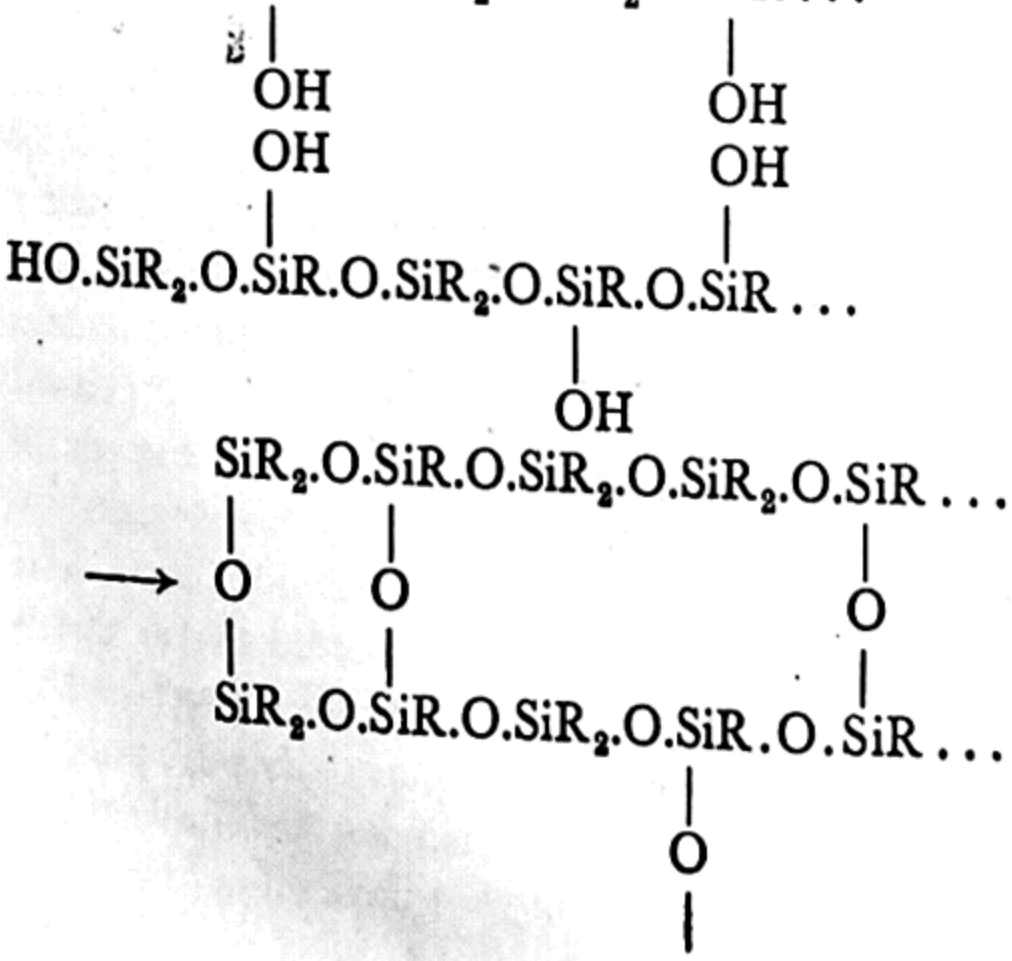
FIGURE 4*b* – *Water flowing down a similar glass plate which has been previously rendered water-repellent by contact with liquid dimethyldichlorosilane. The water runs down the glass with a minimum area of contact, and by continually changing its path produces an effect reminiscent of the violent movement of a serpent.*

An interesting property of certain organosilicon compounds is their ability to produce water-repellent surfaces on glass and ceramics, and to waterproof materials such as paper and cotton [14] which consist chiefly of cellulose (see figures 2, 3, 4). This result may be achieved by a short exposure to the vapour of dimethyldichlorosilane. It is believed that this material reacts with superficial hydroxyl groups and metallic atoms to give a chemically bound, water-impermeable layer of dimethylsiloxane groups. In the case of cellulosic materials it is necessary to neutralise immediately afterwards in order to prevent the harmful action of hydrogen chloride. An alternative and less objectionable method is to impregnate with a liquid polydimethylsilicone and then to subject to a suitable heat-treatment. This is particularly suitable for ceramics, and was employed to safeguard radio and radar equipment against failures due to the deposition of water films on such ceramic parts as coil formers, the bases of high-frequency transformers, and wire-wound resistors.

Paper filters waterproofed in this way were fitted to certain respirators to prevent damage by immersion. It is to be noted that these water-repellent surfaces are eventually obliterated by films of grease and dust. Great care must therefore be taken in their preparation and subsequent treatment; they must not be handled, and should be used only under conditions which substantially preclude contamination.

Silicone resins [15] are produced essentially by condensing a chain-forming intermediate with one capable of cross-linkage; they consist of long-chain molecules which possess a controlled amount of hydroxyl groups. Dissolved in toluene they form viscous varnishes which pass into insoluble coatings when dried and baked.

$HO.SiR_2.O.SiR.O.SiR_2.OSiR_2.O.SiR\ldots$



The baking temperatures are comparatively high (175–250° C), and thereafter the resins may be maintained at 175–200° C for long periods without depreciation. For any given pair of intermediates the amount of cross-linkage must be kept within narrow limits, outside of which the products are of no value as coating materials. This range can be found only by trial, and it will be apparent from the variety of organic radicals that may be present that a great deal of experimentation is necessary to find resins with the desired combination of properties. Those now available have been selected for specific applications. There are insulating varnishes for coating wires, and resins for impregnating glass cloth. Layers of resin-impregnated glass fabric may be bonded together, by heating under pressure, into strong panels or tubes. Other resins may be mixed with thermally stable pigments to give heat-resistant paints and enamels.

The principal object in developing silicone resins was to provide improved forms of insulation for electrical machines such as motors, generators, and transformers [16]. Conventional insulations involve the use of organic varnishes and drying oils, paper, and cotton, and are relatively short-lived when used in heavy-duty machines, particularly those which operate at high ambient temperatures and with occasional periods of overload. Class A insulation, comprising organic varnishes, paper, and cotton, is limited to 100° C, as determined by the resistance method. If the paper and cotton are replaced by glass or asbestos cloth (Class B), the limit is raised to 120° C. From a series of accelerated tests [17] at temperatures up to 300° C it is concluded that insulations based on silicone resins, glass, and asbestos cloth, mica, etc., will permit a limit of 160° C with normal expectations of life. This means a greater degree of freedom for the designer. Silicone insulation is not only heat-resistant but resistant to water and aqueous solutions, and so should find application in mines, and in factories where corrosive chemicals are handled.

The need for a heat-resistant substitute for the rubber insulation on electrical leads has been met by the truly remarkable silicone rubber [18]. This differs from all other rubber-like materials in that its molecular backbone contains no carbon atoms, since it consists of a long chain of dimethylsiloxane groups:

$HO.Si(CH_3)_2.O.Si(CH_3)_2\ldots$

$O.Si(CH_3)_2.O.Si(CH_3)_2.OH$

It is produced from the hydrolysis product of

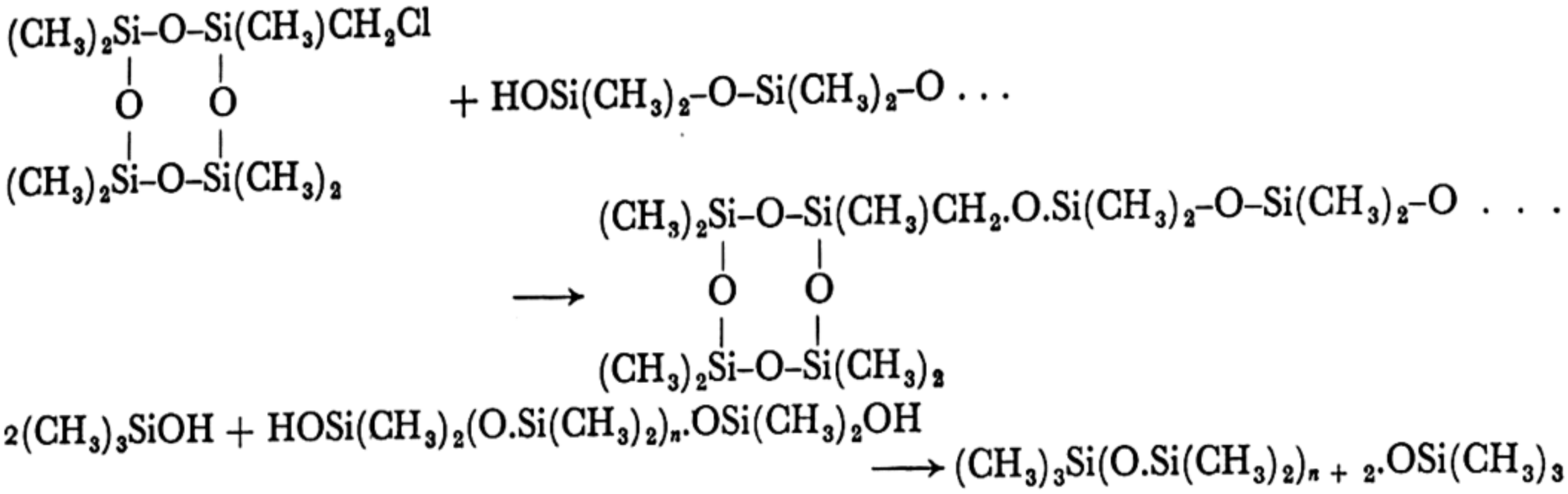
substantially pure dimethyldichlorosilane by heating with hydrochloric acid and the active metallic chlorides, and resembles a translucent gum or sticky jelly. To develop rubber-like properties, cross-linkages must be established between the long-chain molecules by some process of vulcanization, but, as it is saturated, the conventional vulcanization with sulphur is not possible. The method used appears to be one of controlled oxidation, and is probably induced by heating with an organic peroxide. The gum is compounded with suitable proportions of inorganic fillers and vulcanizing agent, and is then moulded, pressed, or extruded at about 150° C. This develops dimensional stability, but the full strength is not attained until after a lengthy cure at 250° C. The tensile strength is lower than that of most other rubbers, being only about 650 pounds per square inch, and the maximum elongation varies between 100 and 300 per cent. The tear-resistance is also poor, but can be improved by incorporating a fabric. Silicone rubber has outstanding heat and oxygen resistance, and has been used extensively as gasket material for joints exposed to temperatures up to 200° C or more.

The erection of the Dow-Corning plant in 1943 was due to a large demand for a material capable of sealing the ignition harnesses of aircraft engines against corona discharge. This trouble is encountered at high altitudes, and may quickly lead to engine failure owing to destruction of insulation. It was found that a grease made by hydrolysing a mixture of silicon tetrachloride, dimethyldichlorosilanes, and methyltrichlorosilanes was eminently suitable for this purpose. It is a colourless, translucent grease which does not change in consistency over the temperature range −40° C to above 200° C, and although its electrical resistance is high it does not form an insulating layer at the disconnectable junctions employed on ignition harnesses. The grease is not only without harmful action on rubber and synthetic insulations but has proved to be a good lubricant and preservative for these materials. When electrical discharge takes place in the grease some carbon is formed, but the principal decomposition product is silica, and so tracking is not as serious as with ordinary organic insulators. The grease was applied to disconnectable junctions and to spark-plug wells in such a way as to exclude air from them. At the same time ingress of moisture was prevented, and so short-circuits due to water films were prevented. During the war silicone ignition-sealing grease contributed in no small way towards the safe operation of Allied aircraft at high altitudes.

The grease found further application in radio and radar equipment, and was used as a lubricant for the shafts and other movable parts of rotating antennae and for the swivel joint in the oxygen supply line to rotating gun turrets on aircraft. It has also been used as a lubricant for the rubber bags used in the low-pressure moulding technique with contact resins. A high-vacuum grease is particularly useful on account of its low vapour pressure, high film strength, and ability to wet all types of surfaces. Special greases thickened with carbon black and with metallic soaps are suitable for lubricating high-speed bearings that must operate at temperatures as low as −75° C or as high as 150° C.

On hydrolysis, dimethyldichlorosilane gives a variety of condensation products of dimethylsilandiol, some being cyclic like hexamethylcyclotrisiloxane (m.p. 65·5° C, b.p. 135° C), while others are linear. Wide variation of molecular complexity is possible, and hence the liquid products cover a wide range of boiling-point and viscosity [19]. These silicone fluids possess many interesting and useful properties; for example, owing to their low molecular cohesion [20] the change of viscosity with temperature is remarkably small. They have high electrical resistance and low power factor up to 10^7 cycles per second. Various artifices are employed to modify and extend the range of available liquids; the viscosity may be increased by heating in air, by boiling with hydrochloric acid, and by condensation with boric anhydride. Other methods are to condense with a lightly chlorinated polymer or with trimethylsilanol (see top of page 35).

In this last process [21] it is claimed that any given condensation product of dimethylsilandiol may be substantially converted into products of selected chain-length by treatment with controlled amounts of trimethylsilandiol, or its anhydride hexamethyldisiloxane, in presence of concentrated sulphuric acid. Owing to their inability to condense further, these end-stopped linear compounds have outstanding thermal stability. Polydimethylsiloxanes may be prepared by an interesting method which avoids the use of pure starting material. The brittle gels obtained by hydrolysing a mixture of dimethyldichloro- and methyltrichlorosilanes are submitted to dry distillation, preferably in the presence of a strong base like sodium hydroxide, when substantially pure polydimethylsiloxanes volatilize, leaving the infusible condensation products of methylsiloxanol behind [22].



Their combination of low viscosity-temperature gradient, wide fluid range, and high compressibility makes certain of these liquid products eminently suitable for use in sensitive hydraulic systems, damping devices, and shock absorbers. Others are effective as mould-release agents, fibre lubricants, and water repellents, and certain exceptionally stable high-boiling products are suitable for use in diffusion pumps, high-temperature baths, and thermally responsive devices. Silicone fluids are remarkably effective in reducing the foaming tendency of hydrocarbon oils, even at dilutions as low as 1 in 10^6.

When delivering the Bakerian lecture to the Royal Society in 1937 Kipping reviewed the organic chemistry of silicon, and concluded with the following words:

> 'Most, if not all, of the known types of organic derivatives of silicon have now been considered, and it may be seen how few they are in comparison with those which are entirely organic; as, moreover, the few which are known are very limited in their reactions, the prospect of any immediate and important advance in this section of chemistry does not seem to be very hopeful.'

That events have proved otherwise is no reflection on his judgment. Doubtless the experimental difficulties with which the subject bristles weighed heavily in the balance, but fortunately human endeavour is cumulative: each new worker starts with vigour and enthusiasm from the advanced bases provided by his predecessors. With characteristic faith, vision, and capacity for intensive work, American investigators and industrialists have been quick to translate the academic results of an English chemist into a fascinating new field of chemical technology. The debut of silicones has been brilliant and full of promise, but their present high cost[1] places them in the luxury class of chemicals. So far, their employment has been restricted to applications in which a valuable advantage can be secured only by making use of their unique properties. Future development must depend on their ability to compete with other new materials on a cost basis, and it may be anticipated that much attention will be given in the near future to the possibility of devising new and cheaper methods for producing the fundamental intermediates.

[1] On the basis of their silicone content, the cost is about seven dollars per pound.

REFERENCES

[1] Friedel, C., and Crafts, J. M. *Ann.*, 1863, **127**, 28.
[2] Ladenburg, A. *Ber.*, 1873, **6**, 1029.
[3] Polis, A. *Ber.*, 1885, **18**, 1540.
[4] Kipping, F. S. *J.C.S.*, 1907, **91**, 209; 1908, **93**, 457.
[5] Kipping, F. S., and Martin, G. *J.C.S.*, 1909, **95**, 302.
[6] Kipping, F. S. *J.C.S.*, 1912, **98**, 101.
[7] Dolgov, B. N. *Uspekhi Khimii*, 1932, 1, No. 5, 626.
[8] Sauer, R. O. *J. Chem. Educ.*, 1944, **21**, 303.
[9] Shtetter, I. I. *Russ. Pat.* 44934, 30th November, 1935.
[10] Andrianov, K. *Zhurnal Obshchei Khimii*, 1938, **8**, 552, 558; *J. Gen. Chem.* (U.S.S.R.), 1938, **8**, 1225; *Org. Chem. Ind.* (U.S.S.R.), 1939, **6**, 203.
[11] Kotow, M. M. *Zhurnal Prikladnei Khimii*, 1939, **12**, (10), 1435.
[12] Rochow, E. G. *J.A.C.S.*, 1945, **67**, 963.
[13] Hurd, D. T., and Rochow, E. G. *J.A.C.S.*, 1945, **67**, 1057.
[14] Norton, F. J. *General Electric Review*, August 1944.
[15] Rochow, E., and Gilliam, W. F. *J.A.C.S.*, 1941, **63**, 798. Hyde, J. F., and DeLong, R. C. *J.A.C.S.*, 1941, **63**, 1194.
[16] Kauppi, T. A., and Moses, G. L. *Trans. Amer. Inst. Elect. Engrs.*, 1945, **64**, 90.
[17] Kauppi, T. A., Grant, G., Moses, G. L., and Horrell, R. F. *Westinghouse Engineer*, September, 1945, 135.
[18] *Silicone Rubber*, General Electric Company.
[19] Corning Glass Works, McGregor, R. R., and Warwick, E. L. B.P. 572331, 572401.
[20] Hunter, M. J., Hyde, J. F., Warwick, E. L., and Fletcher, H. J. *J.A.C.S.*, 1946, **68**, 667.
[21] Patnode, W., and Wilcock, D. F. *J.A.C.S.*, 1946, **68**, 358.
[22] Corning Glass Works and Hyde, J. F. B.P. 571725. Scott, D. W. *J.A.C.S.*, 1946, **68**, 356.

The senses of bats

BRIAN VESEY-FITZGERALD

The remarkable ability of bats to avoid obstacles and catch their prey in the dark has been known for centuries, but it is only during recent years that a convincing explanation has been advanced. There is now a great deal of evidence, based on both laboratory and field research, that bats guide themselves by emitting supersonic sounds and receiving the echoes from objects in their path, a system which has much in common with navigation by radar.

Of all the many problems which bats set for the inquiring naturalist, none has been more puzzling than that presented by their flight at night: the way in which they catch the insects upon which most of them feed (in the case of British bats, upon which *all* of them feed) without colliding with objects in their path. The flight of bats is rapid and the course erratic, frequently through thick woods or the narrow winding passages of caves, often in total darkness. It has always seemed unlikely that animals with such small eyes could see well enough in the dark to fly in such surroundings without mishap. Many experiments have been tried with captive bats to demonstrate their ability to avoid obstacles which they could not see. Towards the end of the eighteenth century the Italian scientist, Lazzaro Spallanzani, found that bats which he had blinded could fly about a room, avoiding the walls, the furniture, and silken threads stretched across their path. A Swiss scientist, Louis Jurine, confirmed this and made the additional discovery that bats lost their ability to avoid obstacles when their hearing was interfered with. Cuvier poured scorn on these findings, and they were forgotten for a century and a half. All that was remembered was that a blinded bat could fly perfectly surely. But the uncanny ability remained, and all sorts of theories were advanced to account for it. It was suggested, for example, that bats were very sensitive to changes in atmospheric pressure.

Then, in 1920, Professor Hartridge suggested that bats when flying in the dark were probably able to ascertain the position of obstacles by means of supersonic sounds emitted by the animals and reflected to their ears. Twenty years later, after the development of radar as an operational system, Griffin and Galambos working in America were able to prove him correct.

Both radar and sonar are, of course, founded on the same fact, namely that if a short burst of energy is sent out and the time taken for the echo to come back is noted, then, if the speed at which the energy travels is known, the distance of the object can be accurately calculated. Moreover, by sending the energy down a narrow beam the bearing of the object can be accurately determined. In radar the energy used is in the form of electromagnetic waves; in sonar (the method by which the depth of water is measured) ordinary sound waves are used. In their direction-finding bats use not audible sound waves, but, as Hartridge suggested and as Griffin and Galambos have proved, supersonic waves. The range of frequencies that a normal human being can hear is from about 16 vibrations a second to about 30,000 a second. Middle C is 256 vibrations a second. The range of frequency of the supersonic waves used by bats is from about 25,000 to 70,000 a second, and is thus mostly above the limit of human hearing.

Griffin and Galambos began their work by confirming that blindfolded bats are able to fly surely. They then confirmed Jurinc's discovery that if the hearing of a bat is impaired it is unable to avoid obstacles when flying. Indeed, they found that a bat with both ears covered is most reluctant to take wing at all, but that a bat with one ear covered will fly with moderate success, though it will be unable to avoid all obstacles. These simple experiments indicated that bats are made aware of the position of obstacles which they cannot see by means of sound waves reflected from them. They then covered the noses and mouths of their bats, but left the ears uncovered, and found that again the animals were unable to fly with certainty. They thus proved that the sound waves reflected by objects must be produced by the vocal apparatus of the bats themselves.

Their further experiments were conducted with the aid of an electronic apparatus known as a supersonic analyser. This consists essentially of













FIGURES 1–3 (*read down*)–*The wing action of a bat in level flight, flying towards the camera. Bats make between fifteen and twenty such strokes of the wing a second, and fly at about ten miles an hour.*

FIGURES 4–6 (*read down*)–*Level flight broadside to the camera. Bats fly by raising the wings partly folded and bringing them sharply down and forward. Note that in all these photographs the mouth is held open.*

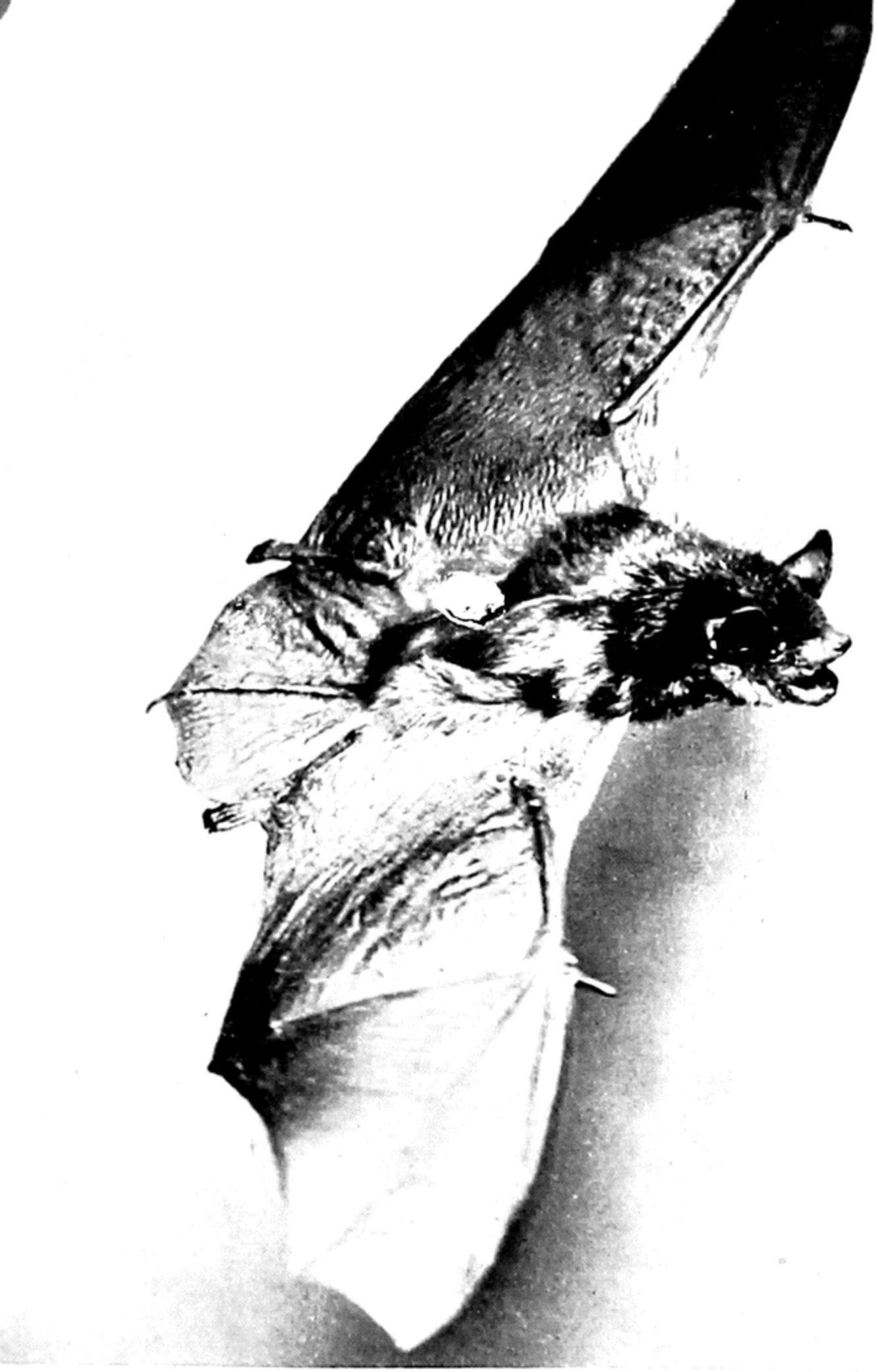


FIGURE 7 – *Warned by the echo, a bat banks sharply to avoid a wall. How close it has come without accident is shown by the shadow.*



FIGURE 8 – *Swooping to alight. Note the depressed interfemoral membrane. All these photographs were taken at* $\frac{1}{100,000}$ *sec.*

a microphone sensitive to supersonic vibrations, a magnifier which amplifies them and converts them to vibrations of a lower frequency, and a recorder which traces a graph on paper when supersonic sounds are received. The analyser measures the frequency of any supersonic vibrations it may pick up. By means of this instrument it was discovered that bats make supersonic sounds at frequent intervals almost all the time. The frequency of the vibrations varies, of course, but it is most usually about 50,000 a second, and at this pitch each squeak lasts for a little less than one two-hundredth of a second.

Now, it is evident that the more frequently squeaks are emitted the fuller the information received. It has been proved that a bat at rest emits a supersonic squeak about ten times a second, but that as soon as it takes wing the rate goes up to about thirty a second. That was to be expected, since a bat on the wing obviously needs more information than a bat at rest. Griffin and Galambos further found that the closer a bat approached an obstacle the faster became the rate of squeaks, rising to fifty and sometimes even to sixty a second, and dropping to normal as soon as the obstacle was passed. The rate of squeak is, of course, governed by the distance from the object, for there must be time for the echo to come back before the next squeak is sent out.

The supersonic tone is not the only sound produced by bats. In addition to the supersonic squeak, which cannot be heard by human beings, they produce three other kinds of sound: (1) the ordinary voice, which is the flight call, and which Hartridge has named the signalling tone; (2) a buzz, which is audible if one is quite close to the animal; and (3) a click, which is usually audible at a distance of several feet. I am not competent to say whether the buzz differs in any way with the species; it sounds exactly the same to me whether emitted by a Serotine (*Eptesicus serotinus*) or a Pipistrelle (*Pipistrellus pipistrellus*), nor can I distinguish any difference between the clicks emitted by the different species. The flight calls, however, are quite distinct. It is possible to distinguish between the species on the wing by means of their flight calls (it is also possible with practice to distinguish between the types of flight), and I have elsewhere attempted to translate the differences between the calls of the various species to paper. It has been shown that the buzz and the click are accompanied by the supersonic tone. In the case of the click there is a single short burst of supersonic energy, but in the case of the buzz there is a continuous evolution of the interrupted supersonic tone. The flight call, however, may be produced by itself or it may be accompanied by the supersonic tone. Some bats, notably the Lesser Horseshoe (*Rhinolophus hipposideros*), have a considerable vocabulary of ordinary sounds, whereas others, notably the Whiskered (*Myotis mystacinus*), scarcely ever make a sound of this sort. I have never heard the Whiskered utter a sound on the wing, and of the many I have kept in captivity only a few have uttered faint grunts, and those very occasionally, when at rest.

How these four different types of sound are produced is not yet clear, but examination of the vocal organs of bats shows that they are very different from those of other animals. The larynx, which in most animals is built of cartilage, in bats is made of bone and is comparatively a massive structure with large and powerful muscles. The strength of the bat's larynx and its small size are obviously well adapted to the production of supersonic sounds, for there must be tremendous energy in the supersonic squeaks as compared with the audible squeaks. The higher the note and the greater the frequency, the greater the energy.

Though it is not yet known exactly how the supersonic vibrations are produced, it is known how the bat avoids hearing the squeak. It is, of course, essential that only the echo should be heard by the bat. The same difficulty had to be overcome in radar transmission. In order to ensure that only the echo is picked up by the receiver, this is suppressed while the transmitter sends. Something of the same kind happens in the bat when emitting the supersonic tone. Griffin and Galambos found that while the squeak is being made a muscle in the ear contracts momentarily, shutting off the squeak, and permitting only the echo to be heard.

Bats are not the only creatures with the power of echo-location. The tapping of Blind Pew's stick is an example of the same process, and many blind human beings develop what appears to be an uncanny ability to move about without striking obstacles. Nor are bats the only creatures able to hear supersonic vibrations: dogs, for example, are often trained on the Galton whistle. But so far as is known at present bats are the only creatures that emit supersonic vibrations and guide themselves by the reflections. This important discovery, however, still leaves unanswered many questions about the behaviour of bats, and, as is the way with important discoveries, poses a number of fresh problems.

Invariably the first question that is asked is: Why do not the bats become confused between the echoes from their own squeaks and the echoes from the squeaks of their neighbours? It might be thought that with a large number of bats of the same species together in a cave or in the roof of a church, and all uttering supersonic squeaks, confusion would be inevitable. But it must be remembered that supersonic squeaks do not travel far, for their energy is quickly dissipated in the air. It has been shown that the supersonic squeaks of bats travel only about fifteen feet, and that they are able to give a useful echo only up to about twelve feet. In other words, provided that the bats are not crammed close together, there is very little likelihood of confusion. But, as everyone with any field experience of bats knows, they very often are crammed close together, yet there is no confusion. It seems evident that there is a difference in the frequency of the vibrations made by each bat. A very slight difference in frequency would be sufficient to enable each bat to recognize its own voice.

There remain a number of problems to which no answer has yet been given. Firstly, do bats emit the supersonic squeak through the mouth or the nose, or both? All the British bats are insect-eaters, and all, with the possible exception of the Barbastelle (*Barbastella barbastellus*), habitually fly with their mouths open. Furthermore, all the British bats capture their prey while in flight, and most of them take flying insects. What happens when the bat closes its mouth on catching an insect? Does echo-location cease (in which case the bat must fly blind) or does it continue through the nose? We do not know. In the Greater Horseshoe (*Rhinolophus ferrum-equinum insulans*) the epiglottis does not open into the back of the mouth as in most animals, but is projected up into the roof of the mouth, fitting into the rear opening of the nasal passages. It is not fixed in this position, and can probably be withdrawn, but the arrangement suggests that the supersonic squeaks, in the *Rhinolophidae* at any rate, are emitted through the nose, and this suggestion receives additional support from the extraordinary skin development on the muzzles of these bats. While the purpose of this appendage, which in some species attains an astonishing complexity, is not known, it has been suggested that it is concerned with directing the squeak into a narrow beam so that the bat's knowledge of its position is greatly increased. Be that as it may, I have no doubt from long personal observation that the Horseshoes have a much finer appreciation of position than other British bats, and especially is this so in the case of the Greater Horseshoe. Indeed, this species is quite uncanny in its judgment of distance. Bats normally hang head downwards, suspended by the toes. It is the usual practice for bats to land head upwards and then to shuffle round until they can get a grip with the toes, but the Greater Horseshoe is accustomed to turning a somersault in the air and gripping straightway with the toes, landing, in other words, in the head-downward position. Very rarely indeed have I seen a bat miss its hold, and there appears to be no slackening of speed as the resting-place is approached. Some of my captive Greater Horseshoes used to sleep under a sideboard, and when they were hanging there was little more than a couple of inches clearance from the floor, yet they would fly under the sideboard, turn their somersaults with absolute certainty, and hang by the toes. And many, many times have I watched this acrobatic performance when they have been hanging from picture-rails and so forth.

There is a marked difference in the structure of the ear in the *Rhinolophidae* and in the *Vespertilionidae*. In the former the pinna is comparatively simple in build, but in the bats without nose-leaves the ear is a much more complex structure, characterized by a great development of a lobe known as the tragus. This is especially well seen in the Long-eared (*Plecotus auritus*), in which species it stands up like a second pinna. It has been suggested that the tragus is in some way connected with echo-location, and the fact that the bats with nose-leaves have no tragus while the bats with the tragus have no nose-leaves is surely significant. It would appear that the two developments must in some way perform similar functions.

It is, I think, noteworthy that the Long-eared, in which there is such a marked development of the tragus, is in comparison with other bats of the same group a master of flight in confined quarters. Most bats, when flying to their feeding-grounds, do so at a considerable height; the Long-eared does so very close to the ground, often at a height of no more than a few inches, and the flight is fast, direct, and confident. Furthermore, the Long-eared captures comparatively few insects in flight, preferring to pick them off the leaves of bushes and trees, a habit which entails the nicest judgment of distance.

Two other British bats, Natterer's (*Myotis nattereri*) and the Whiskered (*M. mystacinus*), have the habit of picking their prey from foliage rather

than taking it in flight. Natterer's is fairly impartial, but the Whiskered very rarely captures a flying insect, preferring to search the hedgerows and fences, especially for spiders, of which it is inordinately fond. Both species have a well-developed tragus, and in both, but more particularly in Natterer's, there is a marked development of the glandular pads on the face.

How bats find their prey is a mystery that has not yet been solved. It is certain that they cannot find it by sight, and there does not seem to be any evidence that their powers of scent are particularly acute. How, then, does the Noctule (*Nyctalus noctula*), flying high and fast, find its prey? If you throw a pebble into the air beneath a hawking Noctule, the bat will dive on to it, swerving away from it at the very last moment without touching it. Attach a fly to a long line and make casts into the air while bats are hawking and you will have them diving at the fly, but it is very unlikely that you will catch one. Daubenton's bat (*Myotis daubentonii*) is sometimes caught on the flies of anglers, but almost always by the wing. I do not think that there has been a single instance of the bat being caught by the mouth, which suggests that at the last moment (but too late to avoid contact altogether) it has realized its mistake. All this suggests that the supersonic squeak sends back an echo from anything flying into or across the path, but it does not explain how the bat knows that that something is worth investigating. Yet I have never seen one bat dive at another, even when there have been many flying at random in a confined area. Nor does it explain how the Long-eared and the Whiskered know that there is an insect or a spider on what their echo-location must have told them is an obstacle to avoid. Yet in a long experience of Whiskered bats, I have not seen one hit a fence or make fruitless visits along a hedge.

One would be inclined to say that the supersonic tone was even more selective than we know it to be were it not for certain things that field experience has brought to notice. I have seen bats of different species collide in mid-air—on one occasion a Noctule with a Serotine (and both animals were killed), and on another occasion a Pipistrelle with a Barbastelle (when the Pipistrelle was killed). These accidents happened during the evening hawking, and one can only suppose that at the time echo-location had stopped, possibly because both animals had captured insects and their mouths were closed.

Field experience shows too that there are times when echo-location does not function at all. I have caught many bats by netting their dens of a summer night. At one time, anxious to discover whether bats flew at night or not—it was at that time thought that they had an evening and a morning flight only—I made a number of all-night watches at dens of Noctule, Whiskered, Pipistrelle, Serotine, and Natterer's, and, after the bats had left the hole for the evening flight, netted the entrance. I caught many bats (and at almost all hours of the night) in the nets, trying to get back to the holes. At that time nothing was known about supersonic vibrations in connection with bats, and I did not think that there was anything odd about it. But in the summer of 1946, realizing that the supersonic tone should have warned them of an obstruction, I repeated the process at dens of Noctule, Whiskered, Daubenton's, and Serotine, with the same result. The bats appeared to be quite unaware that there was an obstruction and flew straight into the nets. Later I covered the entrance hole to a Noctule den with thick brown paper, and even this did not seem to be indicated to the bats, which flew straight into it. Before returning to their den Noctules fly round the tree and in and out among the branches with never a false movement, yet they are unaware of an obstruction at the very entrance to their sleeping-quarters. It seems evident that echo-location, for some reason, is shut off at that moment.

On the other hand, it seems to operate to some extent during hibernation. Everyone who has entered a hibernaculum of bats must have noticed the tremor that goes through the sleeping creatures at the first presence of a stranger. They are asleep, and incapable of movement, but there can be no doubt at all that they are aware.

REFERENCES

HAHN, W. L. *Biol. Bull.*, 1908, **15**, 165.

HARTRIDGE, H. *J. Physiol.*, 1920, **54**, 54.

Idem. Nature, 1945, **156**, 490.

GALAMBOS, R. *J. Accous. Soc. Amer.*, 1942, **14**, 41.

GALAMBOS, R., and GRIFFIN, D. R. *J. Exp. Zool.*, 1942, **89**, 475.

GRIFFIN, D. R. and GALAMBOS, R. *J. Exp. Zool.*, 1941, **86**, 481.

MATTHEWS, L. H., *Zoo Life*, Summer 1946.

SPALLANZANI, L. *Le Opere di L. Spallanzani*, 1932.

VESEY-FITZGERALD, B. *Naturalist*, 1941, 789, 790, 791.

Idem. J. Soc. Pres. Fauna. Emp., 1943, **38**, 10.

Idem. Proc. Hants Field Club, 1944, **16**, 64.

Idem. Discovery, September 1945.

The meaning of resonance in quantum chemistry

C. A. COULSON

The system of equations known as quantum mechanics is unquestionably one of the most important discoveries in the history of science. A particularly interesting chemical application of it is the theory of resonance. This theory, of which a general account is given here, provides a formal and logical explanation of the properties and reactions of a very diverse range of substances. Of outstanding interest is the close similarity between the resonance structures for benzene and those advanced by Kekulé as long ago as 1865.

Resonance in quantum chemistry is a comparatively recent idea, which owes both its birth in 1933 and its early development almost entirely to the work of Linus Pauling in the United States. It is concerned with the way electrons behave in molecules. But before we can understand this we must go back to the individual atoms out of which molecules are formed and ask how the electrons move there; after that, we can discuss their behaviour in simple molecules, and this will lead us almost immediately to the concept of resonance.

The important point about the motion of an electron in an atom is that, since the electron is so very tiny and moves so very fast, we can never measure exactly where it is, and can at best get a kind of blurred pattern. This is quite understandable when we realize that the average velocity of an electron in an atom is at least two million miles per hour, and its orbit is less than one hundred-millionth of an inch across. The shape of this pattern may be calculated mathematically from the so-called Schrödinger Wave Equation. These calculations are quite elaborate, and for our present purposes it is sufficient to say that, although we can never tell exactly where an electron is, we can state that there is a very high probability (e.g. 95 per cent.) that it is within a certain definite volume. Different electrons in an atom will have volumes of different shapes, which they may be said to 'occupy.' In figures 1 and 2 we show these boundary contours for the electrons in hydrogen and oxygen atoms. In hydrogen the one electron lies within a spherical volume of diameter roughly 10^{-8} cm. In oxygen, with eight electrons, two of them (the inner 1*s* or K-shell electrons) have volumes of the same kind but only one-eighth as large; two more (the 2*s* electrons) have spherical volumes of about the same size as in hydrogen; the remaining four (2*p* electrons) lie within boundaries somewhat similar to a dumb-bell or a cottage-loaf in shape. The normal oxygen atom could be pictured as a superposition of all these patterns.

The 'shape' of a molecular electron in a diatomic molecule is not essentially different from

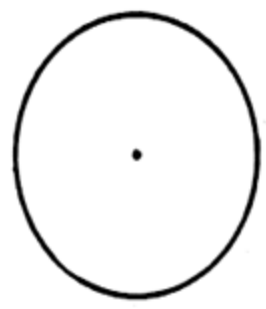


FIGURE 1 (*left*) – *Boundary contour for hydrogen atom.*

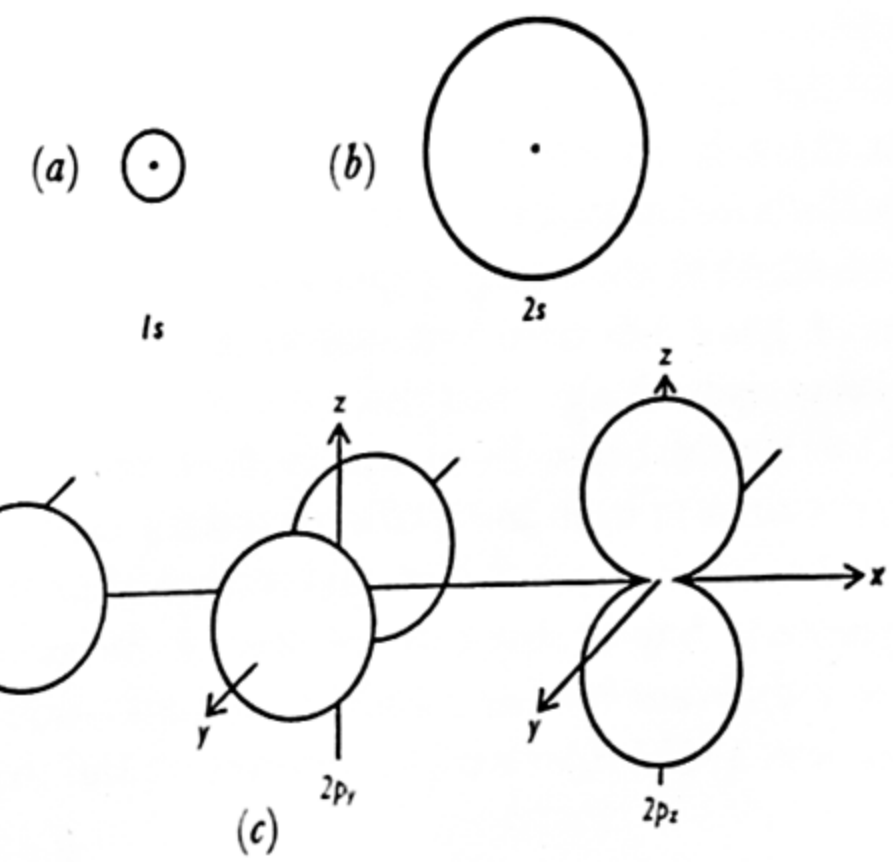


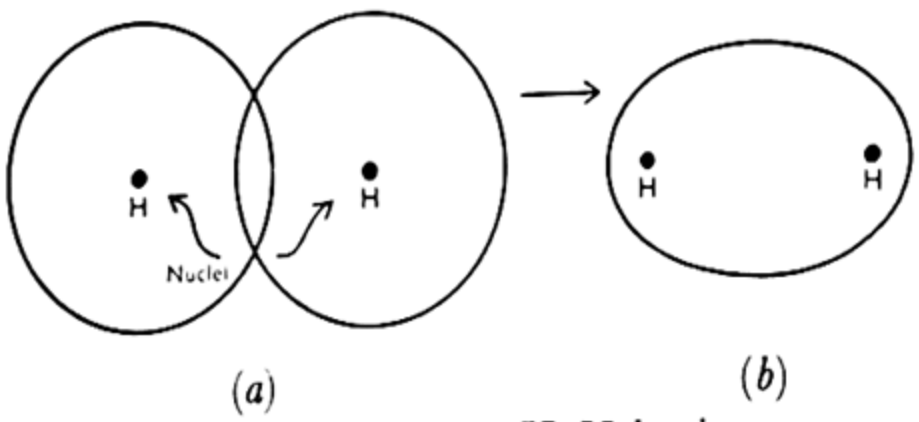
FIGURE 2 – *Boundary contours for oxygen atom. An oxygen atom has its nucleus at the origin and:*

(*a*) *Two electrons in a* 1*s volume.*

(*b*) *Two electrons in a* 2*s volume.*

(*c*) *Two electrons in one of* $2p_x$, $2p_y$ *or* $2p_z$ *and one electron in each of the others.*

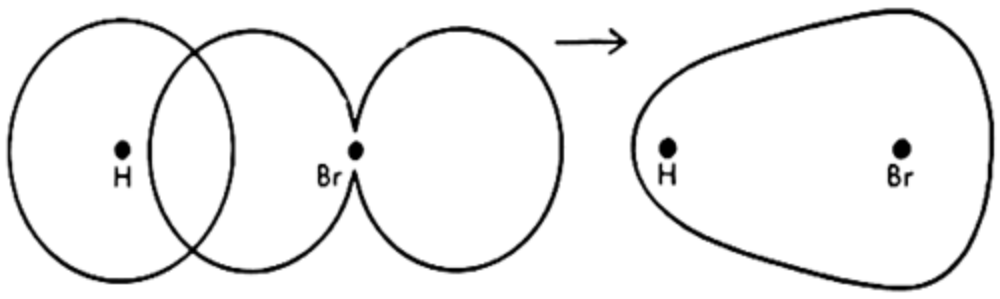
For further description see above.



(*a*) (*b*)

FIGURE 3 – *The* H–H *bond.*

(*a*) *Electron volumes for a pair of isolated hydrogen atoms.*
(*b*) *Electron volumes for a hydrogen molecule. Two electrons in an orbit* (*b*) *comprise the* H–H *bond.*



(*a*) (*b*)

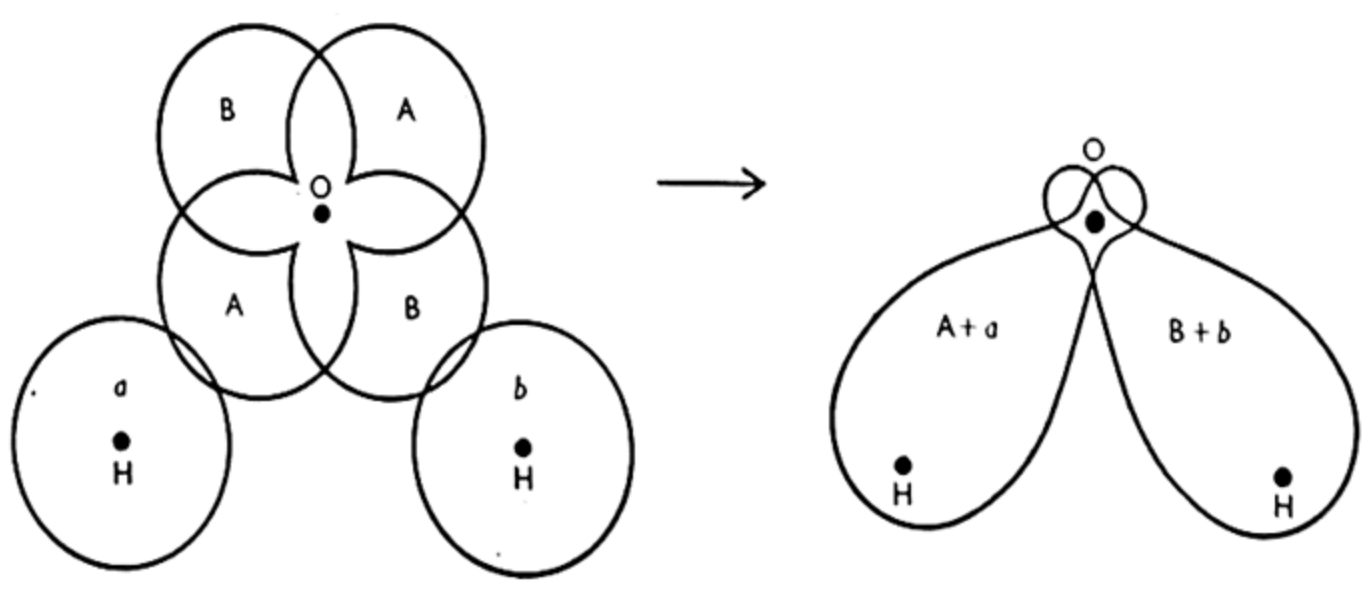
FIGURE 4 – *The* H–Br *bond.*

(*a*) *Electron volumes for isolated hydrogen and bromine atoms.*
(*b*) *Electron volumes for* H–Br *bond electrons. Two electrons in an orbit* (*b*) *comprise the* H–Br *bond.*

that of an atomic electron. The first important characteristic, originally noted by G. N. Lewis in 1916, is that it requires two electrons to establish a single bond between two atoms, as in H_2 or HCl, and four electrons for a double bond, as in O_2. The exceptions to this rule, which are called the 'odd molecules,' such as NO, are odd in more senses than one, and need not be considered in a preliminary account of the theory of chemical binding. The second characteristic is that electrons not involved in the formation of a bond have distinguishing patterns almost identical with those in isolated atoms. When describing the orbits of electrons in molecules, therefore, we need concern ourselves only with those electrons which actually form the bond. These orbits will be similar in general terms to the atomic patterns, except of course that they include two nuclei and may be called bicentric. They are to be interpreted as meaning that although we cannot precisely define the position of these valency electrons, each one is, for practical purposes, effectively confined within a certain contour whose shape may be determined mathematically. Figure 3 (b) shows the contour for molecular hydrogen (H_2), from which we see that the H–H bond is due to two electrons whose orbits distribute them fairly uniformly within a symmetrical sausage-shaped volume. This figure also shows how closely the molecular pattern may be regarded as compounded out of the separate isolated atomic patterns shown on the left. Figure 4 shows how the bond in HBr derives from a molecular pattern composed of a hydrogen 1*s* pattern (as in figure 1) and a bromine 4*p* pattern somewhat similar to that shown in figure 2 for oxygen. Once again the molecular pattern is symmetrical around the axis of the bond, though now, on account of the greater electron-attracting power of the bromine atom, it leans over more to the bromine end of the bond. Two electrons in a bond pattern such as figure 3 or 4 are said to be paired together; in quantum-mechanical language they have their spins opposed to one another. Together they may be said to form an electron-pair bond.

With polyatomic molecules a similar situation occurs. Each bond is formed by two electrons, which are paired together. These each have a pattern which embraces two atomic centres and is closely equivalent to a combination of atomic patterns from the two atoms concerned. The atomic orbits which are thus synthesized into a molecular orbit are always those which overlap one another as much as possible. This, though there is no space to elaborate it here, is really the basis of the theory of valency, and enables us to predict the characteristic valency angles of stereochemistry. Figure 5 shows how the two O–H bonds in water (H_2O) are approximately at right angles, and how they are formed by synthesis of a hydrogen 1*s* pattern and an oxygen 2*p* pattern.

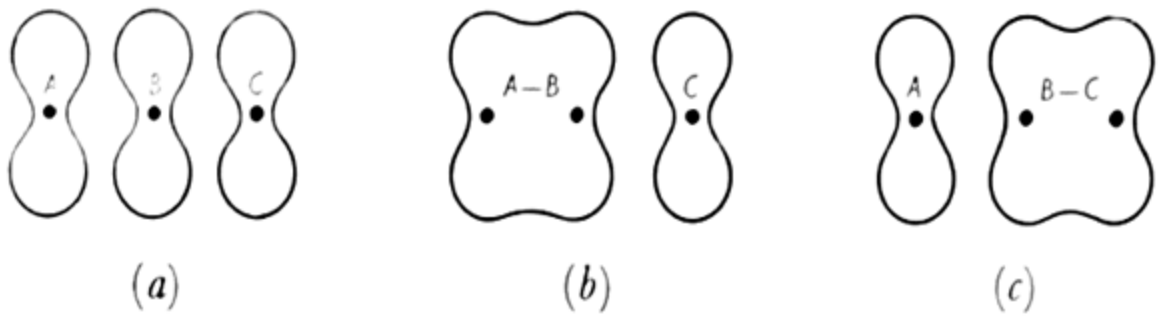
This brings us to resonance itself. As a rule,



(*a*) (*b*)

FIGURE 5 – *The water molecule.*

(*a*) *The separate atomic electron patterns.*
(*b*) *The molecular electron patterns.*
Two electrons in each pattern $A + a$ *and* $B + b$ *give rise to the two* O–H *bonds.*



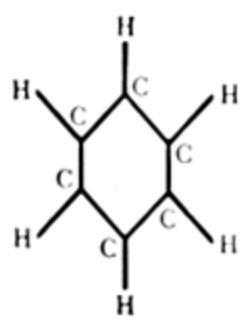
(*a*) (*b*) (*c*)

FIGURE 6

(*a*) *Three isolated unpaired atomic patterns.*
(*b*), (*c*) *Alternative pairings to form molecular patterns.*

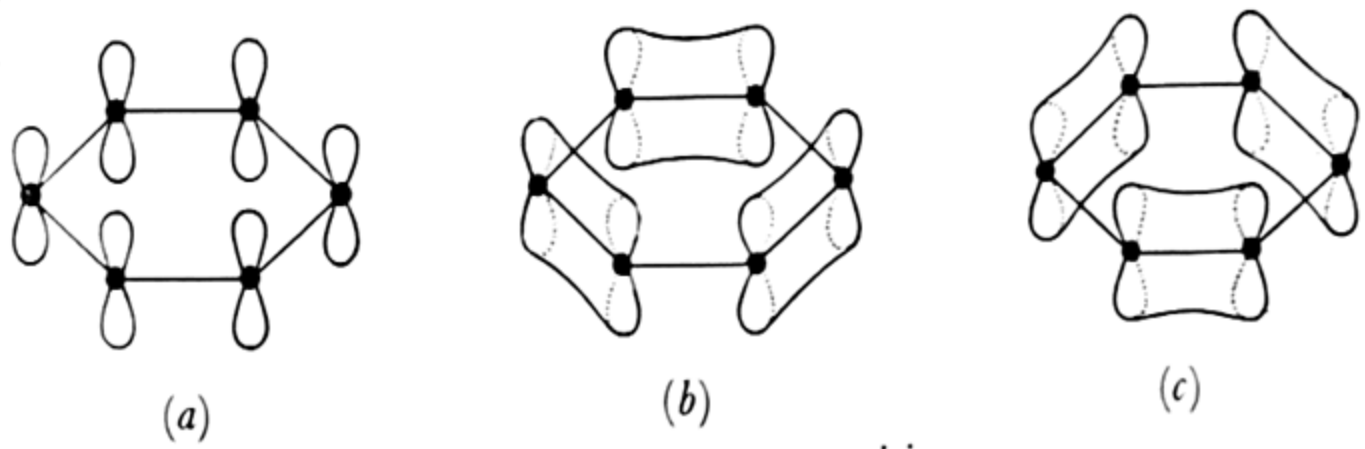
there is no difficulty in saying how the atomic patterns are combined to form molecular patterns localized between two nuclei and giving rise, if there are two electrons concerned, to a normal single bond, and if there are four electrons, to a normal double bond. The criterion that the component atomic patterns are to overlap as much as possible is a sufficient guide. For example, in figure 5 it would be illogical to combine the oxygen pattern *A* with the hydrogen pattern *b*, since the two patterns scarcely overlap at all, whereas oxygen *A* and hydrogen *a* do overlap fairly considerably. But there are occasions when this combining together of atomic orbits is not so unequivocal. For suppose (figure 6*a*) that we have three atomic 2*p* patterns (dumb-bell orbits *A*, *B*, *C*) on adjacent atoms, and that the three patterns are similar and parallel, and point perpendicularly to the line of atomic centres. We are to make molecular patterns from these three atomic ones. Clearly one way is to link *A* and *B* and so make a molecular pattern such as figure 6*b*, in which *C* is left just as in an isolated atom. But equally clearly there is another alternative (figure 6*c*), where we link *B* and *C* and leave *A* isolated. Nobody can say that one of these is favoured rather than the other. In a word, the two possibilities (*b*) and (*c*), which Pauling calls Valence-Bond Structures, are both equally possible: there is no unique pairing of the atomic electrons.

An extreme case—indeed, the *locus classicus* of the phenomenon—occurs in benzene (C_6H_6). This molecule is known to be planar and in the shape of a regular hexagon, thus:



A pair of electrons is allotted to a sausage-like pattern between all adjacent C–C atoms and between all C–H atoms, thus forming a total of twelve normal single bonds. There still remain the six dumb-bell patterns for an atomic electron around each carbon nucleus. These are shown schematically in figure 7*a*. Now, there are obviously two quite distinct ways of joining these in pairs: in a manner exactly equivalent to that illustrated in 6*b* and 6*c* we obtain the molecular patterns 7*b* and 7*c*. Once again there is no unique way of pairing the atomic electrons, for 7*b* and 7*c* are obviously on an entirely equal footing. The mathematical reasoning of quantum theory now tells us that neither of the two structures 7*b*, 7*c* is by itself a valid representation of the appropriate Schrödinger wave function, but a good approximation is obtained if we suppose that both structures contribute equally to a so-called resonance hybrid. Physically this means that benzene should behave partly as if the double bonds were in the one position and partly as if in the other.

But notice what our mathematics implies. For the two structures 7*b*, 7*c* are precisely what Kekulé introduced as long ago as 1865; and he supposed them to be in dynamic oscillation, interconversion taking place too quickly to be observed. Now we see that the phenomenon described as resonance means that instead of two structures alternating rapidly, we must regard the true situation as a simultaneous superposition of both. The bonds do not alternate between single and double: they are at the same time partly single and partly double, according to the way the electrons are paired. Our mathematics has taken Kekulé's original brilliant intuition and fitted it into a formal, logical, and precise theory. An interesting verification of this point of view is given by the carbon–carbon bond length. On Kekulé's picture this would alternate between 1·54 Ångstroms (single C–C bond) and 1·34 Ångstroms (double C = C bond). According to the resonance theory, in which all bonds are equivalent, it should have



(*a*) (*b*) (*c*)

FIGURE 7 – *Benzene pairings.*

(*a*) *Separate unpaired electron patterns.*
(*b*), (*c*) *Distinct alternative pairings to form molecular patterns.*

one distinct length between these two. X-ray measurements show it to be about 1·39 Ångstroms.

Before going any farther we can now give a more inclusive definition of quantum-mechanical resonance. 'When the electrons in a molecule may be paired together in two or more structures which are equivalent or nearly equivalent to one another, the actual molecule does not conform to any one of the structures, but is a resonance hybrid of them all, showing at the same time characteristics of each separate structure.'

Why is it called resonance? Historically the name derives originally from the acoustic phenomenon. Resonance can be illustrated mechanically by the familiar physical experiment in which two simple pendulums of nearly equal lengths are swinging side by side suspended from the same taut horizontal wire. If the two natural periods are nearly equal, it is well known that the two separate oscillations interact and are replaced by two combined modes (normal modes) of vibration, in which the energy flows from one pendulum to the other, so that the amplitude of the one decreases while that of the other increases, and then vice versa. The parallel with benzene is very obvious. Each separate pendulum oscillation corresponds to a particular pairing scheme *7b* or *7c* which interchanges with the other. In fact, there is a further important comparison, for there are two possible normal modes for the pendulums. One frequency is greater and the other is less than that of the two components. In the case of benzene there are two ways of superposing the structures *7b* and *7c*: one has a lower energy than either structure by itself; the other has a greater energy. We call the resonance hybrid with lower energy the ground state, and the lowering of energy as a result of the superposition of the separate structures is called the resonance energy. Other things being equal, the resonance energy is greater the more structures there are combining. In the case of benzene the upper state is important in absorption of light, and the characteristic appearance of the compound is related to the emission or absorption of light when a quantum jump takes place from the one resonance hybrid to the other.

All this is quite general. On the one hand, there is always a lowering of energy as a result of resonance mixing, which nicely accounts for the relatively great stability of compounds like benzene. On the other hand, this is achieved by delocalizing the electrons. In the case of benzene, on account of the superposition of *7b* and *7c* an electron originally round atom No. 1 is sometimes paired in a molecular orbit round atom No. 2, so that it can migrate to this atom. In the new position it may be paired with an orbit from atom No. 3, and may thus continue its migration round the carbon ring. Indeed, we might describe the situation by saying that there are six electrons in benzene which are able to flow as tiny currents round the central hexagon. These currents should show characteristic magnetic effects. Without describing them in detail it may be said that these are just what are found experimentally in the diamagnetic anisotropy. This delocalizing of electrons should also mean that any chemical disturbance at one part of the ring should be propagated (with perhaps a diminishing power) to all other parts of the molecule. This is, in fact, the basis of the theoretical explanation of all the inductive and mesomeric effects so fully investigated by experiments in which one atom or group is replaced by another.

These are important applications of the theory of resonance, but they by no means exhaust its utility. There is space briefly to list five others, in which we choose particular examples to illustrate general principles.

FRACTIONAL BOND ORDER; EXAMPLE, NAPHTHALENE

In benzene there are only two important structures. In naphthalene, however, there are three, as shown in figure 8, corresponding to the three different ways of pairing the atomic electron patterns. If all three of these contribute equally to the resonance hybrid (this is not quite accurate, but it is not far wrong), a bond such as that marked *A* would be a double bond for $\frac{2}{3}$ of the time and a single bond for $\frac{1}{3}$. More accurately, it would be described as $\frac{2}{3}$ of a double bond and $\frac{1}{3}$ of a single bond. We might call its order $1\frac{2}{3}$. Similarly the bond *B* should have an order $1\frac{1}{3}$. Clearly *A* would be more similar to a double bond. This fits very satisfactorily with the experimental fact that *A* is more reactive than *B*. But notice that we are now able to assign a numerical (fractional) order to a bond. One result of resonance is to destroy the pure single-bond or pure double-bond

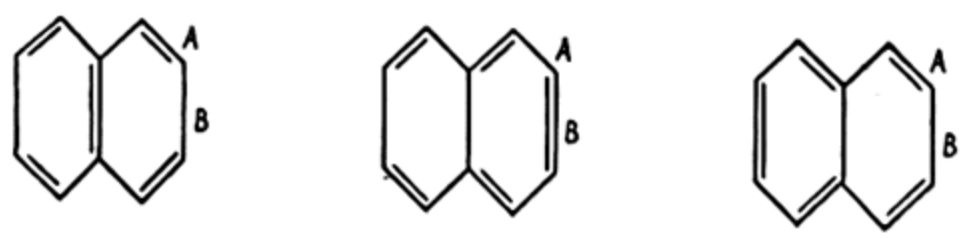


FIGURE 8 – *Three valency bond structures for naphthalene.*

character of a bond and to replace it by a fractional bond order.

IONIC STRUCTURES: EXAMPLE, THE CARBONYL GROUP

Sometimes resonance is confined to a part of a larger molecule. Thus, if R stands for some large saturated radical (in which resonance is not a very significant factor), the molecule R·COOH is an acid; in solution H^+ separates off, leaving a structure that might be represented by the diagram $R\text{–}C\langle^{O}_{O^-}$, in which a free electron is found on the one O atom. But another pairing system would lead to the structure $R\text{–}C\langle^{O^-}_{O}$. These are called ionic structures to distinguish them from the previous covalent structures. Evidently there is resonance between the two ionic structures. The resulting resonance energy is one strong reason for the acidic property of the original molecule, for it makes the removal of the H atom (without its electron) relatively easy.

METALLIC CONDUCTIVITY: EXAMPLE, A GRAPHITE LAYER

We have just seen how ionic structures contribute to resonance. Their existence also explains how a metal is able to conduct electricity, i.e. how electrons can move with greater or less freedom over a regular lattice of atoms. Consider in particular a small element $AB \ldots F$ of a layer of graphite, shown in figure 9, in which the carbon atoms are arranged in a regular hexagonal array and which is bounded by the electrodes of a battery at XX' and YY'. We can draw a series of resonance structures to illustrate the pairings of electrons, just as we have already done for benzene in figure 7. Figures 9*a* and 9*b* are two examples from a very large number. Then on account of the alternative electron pairings represented by 9*a* and 9*b*, an electron originally at X can move first to A, then to $B, \ldots$, and finally to Y. So electrons are able to move quite freely through the lattice. The only difficulty is that, so far, whenever one electron moves in one direction another electron momentarily paired with it must move in the opposite direction, so that there is no net flow of charge. To get such a flow we must introduce ionic structures like 9*c*, in which there is an extra electron on atom F at the expense of atom A. Normally this structure will be balanced by another, with the charges interchanged. But in the presence of a suitable electric field c will predominate and there is a partial flow of charge. If the electrodes of the battery are able to collect this charge at YY' and re-issue it to the crystal layer at XX', we can understand why the applied e.m.f. is able to cause a steady flow of current. Ohm's law is therefore bound up with the relative importance of ionic structures such as 9*c*.

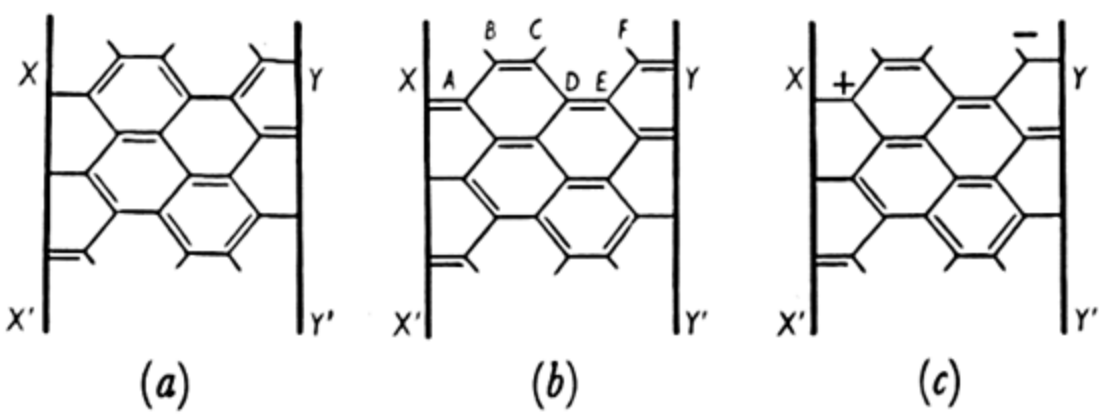


FIGURE 9 – *Bond structures for a graphite layer.*
(*a*), (*b*) *Alternative covalent structures.*
(*c*) *An ionic structure.*

CHEMICAL REACTIONS: EXAMPLE, $H_2 + Br_2 \rightarrow 2HBr$

Resonance also enables us to understand what is happening in a chemical reaction. Consider the reaction $H_2 + Br_2 \rightarrow 2HBr$. In figure 10*a* we show the H_2 and Br_2 molecules approaching one another in such a way as to facilitate the conversion to two HBr molecules shown in (*e*). The original interpretation of this reaction, due to Erlenmeyer (1901), was that as the H_2 and Br_2 approached, there came a sudden moment when the bonds switched over and instead of H–H and Br–Br we discovered two molecules of H–Br. But now we see that there is no sudden switching of the bonds: there is a gradual transition. In (*b*) the structure $\begin{matrix} H & Br \\ | & | \\ H & Br \end{matrix}$ contributes more than $\begin{matrix} H\text{–}Br \\ H\text{–}Br \end{matrix}$. But in (*c*) they contribute equally to the resonance hybrid. This latter situation is sometimes called

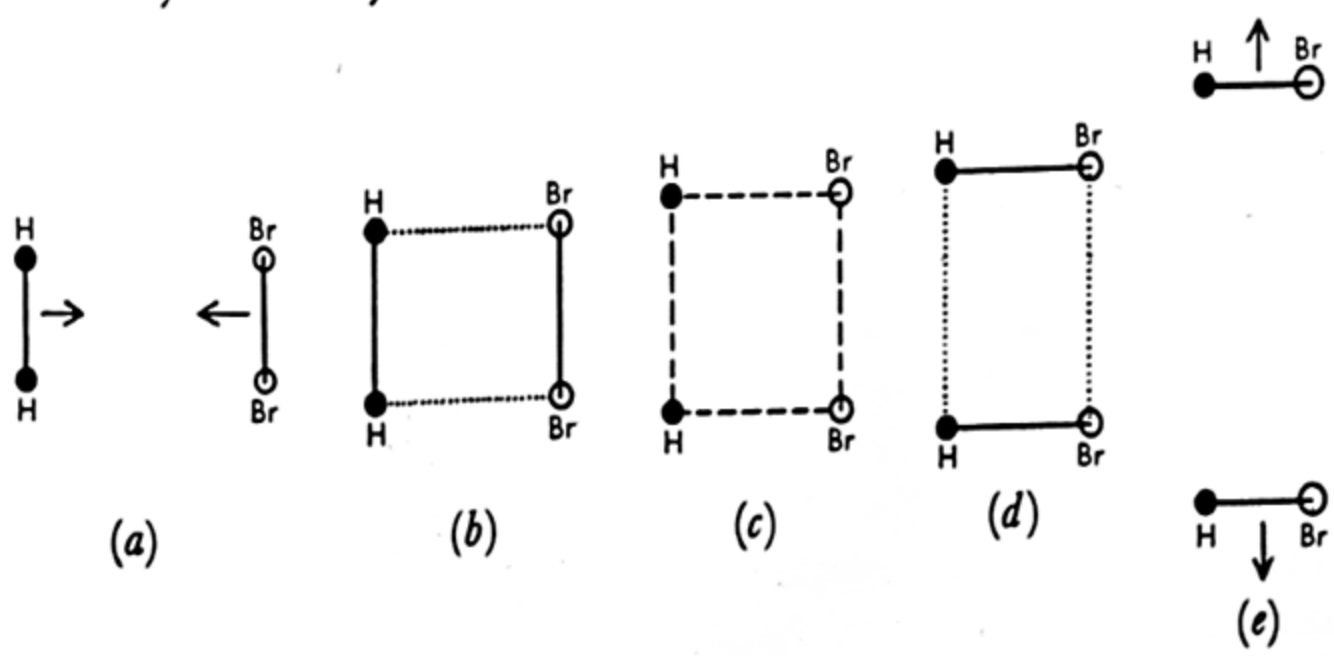


FIGURE 10 – *Successive stages in the reaction* $H_2 + Br_2 \rightarrow 2HBr$.

the Reaction Complex or Activated Complex: in it the bonds are scarcely localized at all. As the reaction proceeds, in (*d*) the $\begin{matrix}\text{H–Br}\\ \text{H–Br}\end{matrix}$ structure is dominant, till finally in (*e*) two H–Br molecules are existing completely in their own right, and the reaction has taken place.

POLYMERIZATION: EXAMPLE, POLYTHENE

A closely similar explanation can be given for polymerization reactions, so important in the study and development of artificial rubber. Below (figure 11) we show the first stage in the polymerization of ethylene to polythene. As two ethylene molecules (C_2H_4) approach together

(I) $H_2C = CH_2$ $H_2C = CH_2$

(II) $---H_2C - CH_2 - -$ $- - H_2C - CH_2 ---$

(III) $- H_2C - CH_2 - CH_2 - CH_2 -$

FIGURE 11 – *Stages in the polymerization of ethylene.*

there is a small amount of resonance between the structure (I), with two localized double bonds, and (II), in which the double bonds have been opened up and pairing takes place across the central carbon atoms. As the molecules approach more closely (II) becomes increasingly important, so that we finish with (III), in which the free valency at either end of the chain makes the subsequent addition of more ethylene units at least as easy as the first.

But enough has been said to show the wide application of the concept of resonance. One last question arises: is resonance a *real* phenomenon? The answer is, quite definitely, no. For consider benzene, with its two Kekulé structures 7*b*, *c*. We cannot say that the molecule has either one or the other structure, or even that it oscillates between them. There is, in fact, simply the C–C aromatic bond. Putting it in mathematical terms, there is just one full, complete, and proper solution of the Schrödinger wave equation that describes the motion of the electrons. Resonance is merely a way of dissecting this solution: or, indeed, since the full solution is too complicated to work out in detail, resonance is one way—and that not the only way—of describing the approximate solution. It is a 'calculus,' if by calculus we mean a method of calculation; but it has no physical reality. It has grown up because chemists have become so used to the idea of localized electron-pair bonds that they are loth to abandon it, and prefer to speak of a superposition of definite structures, each of which contains familiar single or double bonds and can be easily visualized. Like most good things, the idea can be overworked, but no-one can deny that in the years since 1933 it has proved extraordinarily successful in correlating, explaining, and even predicting an astonishingly large and varied body of chemical experience.

Book reviews

FRONTIERS OF ASTRONOMY

Frontiers of Astronomy, *by David S. Evans. Pp.* 174, *with* 8 *plates and* 47 *diagrams. Sigma Books Ltd., London.* 1946. 6*s. net.*

Dr Evans has achieved a considerable measure of success in the difficult task of endeavouring to explain in simple terms, which the general reader can understand, some of the problems with which astronomers are concerned today and why solutions to these problems are required. In a slender book, such as this, it is possible to deal only with selected topics and the particular choice of topics is naturally conditioned to some extent by the personal interests of the author. It is therefore perhaps ungenerous to criticize the choice of subject matter. Reference might have been made to some of the unsolved problems of the solar system. It is true that the centre of gravity of astronomical research has moved away from the solar system (the sun excepted), and the reader may conclude that there is nothing more to be learnt. But the problems of the origin of comets, of the nature of the clouds of Venus, of why Venus has no water while the earth has plenty, of the nature of the markings on Jupiter and of the colours of its belts, of the sudden brightening and fading of certain comets, all need solutions and are but a few of the problems of the solar system. The sun's corona is now being intensively studied and undoubtedly holds the key to many solar problems; more might have been said about this and about the magnetic fields of sunspots, which are invariably involved in the production of solar flares. The fact that no mention is made of astronomical investigation by radio and radar — electromagnetic radiation from the sun and the Milky Way giving rise to radio noise, radar reflections from meteors, etc.—is merely a reminder that astronomy advances so fast that any book dealing with its frontiers is necessarily somewhat out of date before it leaves the publishers.

H. SPENCER JONES

DIFFRACTION BY MOLECULES

The Diffraction of X-rays and Electrons by Molecules, *by M. H. Pirenne, with a foreword by P. Debye. Pp. xii + 160. Cambridge University Press.* 1946. *12s. 6d. net.*

This book deals chiefly with the theory of the diffraction of X-rays and electrons by atoms and molecules, and the use of diffraction methods for the determination of the geometry of simple gas molecules. It is a book about physical principles and methods rather than results. The exposition is admirably clear and concise, and the subject matter will interest not only specialists in the subject but also a wider circle of readers. All X-ray diffraction workers, for instance, will find very useful the earlier chapters on coherent and incoherent scattering, fluorescent radiation, and atomic scattering factors for X-rays; the general reader will be grateful for the discussion of the relative merits of X-ray and electron diffraction methods for studying gas molecules, and will, it is to be hoped, agree with the author's conclusion that both methods should be used for certain types of molecules. If one suggestion may be offered it is this. In Dr Pirenne's book, much less space is given to electron than to X-ray diffraction, although in fact it is the electron method that has been the more widely used of the two for the study of gas molecules. This preferential treatment of X-rays is understandable, because X-ray diffraction is the author's own field of original work, but the book would be better balanced, and would fulfil more adequately the expectations aroused by its title, if the two subjects were treated on an equal footing. Perhaps, however, one should not question a writer's scope, but only sympathize with his difficulty in finding a suitable title for his work. Altogether, this book is a very welcome addition to the literature of diffraction methods.

C. W. BUNN

SCIENCE AND NUTRITION

Science and Nutrition, *by A. L. Bacharach. Pp. 142. C. A. Watts & Co. Ltd., London. Second edition,* 1945. *5s. net.*

The second edition of this book should be as popular as the first. The author has undoubtedly fulfilled his purpose of putting before the reader an account of the methods used in the laboratory for exploring nutritional problems and of the knowledge thereby obtained. He has done it with a simplicity of phrase and use of apt simile that facilitate assimilation. Nowhere does his intention to treat nutrition from the standpoint of the chemist cause him to overlook the nutritional value of substances, even if their chemical complexity be that of the essential oils.

This edition adopts the well-planned arrangement of the first, and incorporates much new material. After a brief account of the form of animal experimentation is a description of the basic constituents of diet: the proteins, fats, and carbohydrates. Two more sections deal with minerals and vitamins. The subject matter is chosen with care and includes only such recent findings upon amino acids, trace elements, and newly isolated vitamins as can be accepted without doubt.

In applying to man the results obtained with laboratory animals the author emphasizes the need for caution. Yet they do suggest that malnutrition in man can arise from a multitude of causes and can be responsible for as much ill-health as infection. As a remedy the author describes in the last section of his book an optimal diet, in the design of which he has combined commonsense with laboratory results; he advocates that all should have the means to obtain it. His book should provide that instruction upon nutrition which will ensure that the means are wisely spent.

J. R. P. O'BRIEN

PRACTICAL CHEMISTRY

Practical Chemistry for Medical Students, *by William Klyne. With a foreword by Professor G. F. Marrian. Pp. xvi + 460. E. & S. Livingstone Ltd., Edinburgh.* 1946. *20s. net.*

It has now become recognized that the education of the future physician must be based on a sound scientific background, particularly as regards chemistry. Within the 460 pages of this excellent book, the author has provided an experimental course of study of an ample and varied character. The book is divided into five parts entitled: Some Fundamental Scientific Ideas, Practical Methods, General and Physical Chemistry, Inorganic Chemistry, and Organic Chemistry. In his preface the author emphasizes that the time allotted to chemistry at Edinburgh does not provide for more than half of the work in the book to be covered. One can only remark that so long as the right choice is made, the interests of the student are amply safeguarded.

Great care has been taken to ensure that the student shall approach his experimental work in the right spirit, not only as regards understanding of theoretical principles, but from the standpoint of care and exactness in carrying it out. But the reviewer is inclined to wonder whether the elaborate list of directions on pages 23–25, concerning what is and what is not to be done in matters of manipulation, could not have been entrusted to demonstrators. Criticism may be directed to some features of the chapter on volumetric analysis, e.g. titration values of less than 10 ml. on page 132, and the omission of the use of adsorption indicators. On page 424 the author refers to Gerhardt's test for aceto-acetic acid. Presumably he means Geuther's test, since Gerhardt died in 1856, and aceto-acetic ester was discovered by Geuther in 1863.

A. J. BERRY

RELIGION AND SCIENCE

The Fourfold Vision, *by F. Sherwood Taylor. Pp. 108. Chapman & Hall Limited, London.* 1945. *6s. net.*

Dr Sherwood Taylor sets out to show that the knowledge and methods of science are not contrary to religion but may indeed contribute thereto. It is an attempt that has been made by many others, with varying degrees of success, but the present essay is devised especially for the scientist, and largely neglects metaphysical arguments familiar to the philosopher and theologian. The main thesis, from which the book takes its title, is that man can achieve four means of apprehension of nature, of which the scientific is but one: first the mere apprehension of diversity without unity; then the perception of the beautiful in nature and its integration in art; next the discovery of harmony in the order of nature through science and philosophy; and finally the apprehension of the world as unified in its orientation to God. Dr Taylor marshals his arguments with great skill and will carry his readers along with him for a certain distance—indeed a considerable distance. But the central problem is perhaps of its nature insoluble, and one cannot help feeling that the book will strengthen the conviction of those already convinced rather than convince those who are not.

ENDEAVOUR

A quarterly review designed to record the progress
of the sciences in the service of mankind

VOLUME VI APRIL 1947 NUMBER 22

The role of the scientific society

Progress in all branches of learning is dependent upon the exchange of information between workers pursuing similar lines of study. Such an exchange is of particular importance in science, where the aim is primarily to collect facts and to interpret them in terms of general principles. Science is exceptional in that its interpretation is comparatively little influenced by the opinions of individuals. While theories may need to be revised or even abandoned altogether as new facts are discovered, the facts themselves remain as permanent aids to future workers. The progress of science is therefore essentially a cumulative one, and the modern scientist can normally build his own work on the foundations established by his predecessors. This stability is lacking in branches of learning where interpretation is coloured by personal, national, or political bias. In literature, music, or painting, for example, the accepted standards of one generation may be—and frequently are—scorned by the next.

The progress of science having been so dependent upon the rapid exchange of new knowledge between workers in the same field, scientific societies, of which the main purpose is to facilitate this exchange, have proved of great historical importance. They were formed in some sort almost as soon as experimental science became established. Crafts and guilds for the handing on of technical knowledge from one generation to another are, of course, almost as old as civilization itself, but as their purpose is rather to preserve existing knowledge than to extend it they can scarcely be considered as scientific societies in the accepted sense.

One of the earliest scientific societies of which we have certain knowledge was that of the Ikhwān al-ṣafā', or Brethren of Sincerity, established at Basra about 983, which endeavoured to reconcile Greek science with the Koran. The members discussed scientific, philosophical, and mathematical subjects, and wrote a series of fifty-two treatises which comprised a sort of encyclopaedia. Seventeen of these treatises dealt with natural sciences and fourteen with mathematics and logic. The interests of the Brethren of Sincerity had much in common with those of the philosophers who, centuries later, formed the Royal Society in London. They sought explanations of tides, eclipses, earthquakes, and other natural phenomena, and recognized, for instance, that sound is produced by vibrations of the air, though they could offer no satisfactory explanation of why simultaneous sounds do not mix.

In Europe, the earliest scientific societies were formed in Italy. In 1560 Giambattista della Porta founded the *Academia Secretorum Naturae* at Naples, membership of which was conditional upon making some discovery in natural science. Porta himself made many important physical observations. He recognized the heating effect of light rays and may also have been the first to use a lens in a camera obscura. In 1603 the *Academia dei Lincei* was founded by Federigo Cesi, Marchese di Monticelli. Among its earliest members was Galileo. The *Accademia del Cimento* was founded at Florence by Leopold de' Medici in 1657. It was an institution for experimental research, and though it lasted for only ten years its reports, published in 1667, form a landmark in the history of science. Torricelli and the physiologist Borelli were among the members of the *Cimento*.

In France the *Académie des Sciences* (1666) evolved from the frequent meetings of a group of scientists, including Descartes, Gassendi, and Pascal. This informal club was eventually given official status as a result of the interest taken in it by Colbert, and Louis XIV made grants of money to it and to its members. Later members included Laplace, Buffon, Jussieu, and Lavoisier. The

Russian Academy of Sciences, founded in 1724, was modelled on the French *Académie*.

In Britain the need for a society for the discussion of scientific matters began to be felt early in the seventeenth century, when the meetings at Gresham College of John Wallis, J. Wilkins, J. Goddard, C. Ent, Robert Boyle, W. Petty, and others resulted in the formation of the Philosophical or Invisible College. From these meetings originated the Royal Society (granted its first Royal Charter by Charles II in 1662), which is today by far the most celebrated scientific society in the world. The Manchester Literary and Philosophical Society, which numbered John Dalton among its many distinguished members, was founded in 1781.

These early scientific societies were representative of science as a whole, for though their members might have a particular interest in physics, chemistry, biology, etc., they were in general natural philosophers with catholic interests. The rapidly increasing extent of scientific knowledge, however, compelled scientists to devote their attention chiefly to one only of the main branches of science. By the end of the eighteenth and the beginning of the nineteenth century, scientific societies appropriate to these specialized interests were being formed. Typical of them were the Geological Society (1807) and the Astronomical Society (1820). In this issue we publish an article on the Chemical Society (1841), which is celebrating its centenary this year after a delay occasioned by the late war. Similar societies were formed on the Continent. The French Chemical Society was founded in 1857 and the German Chemical Society in 1866–7.

The value of scientific societies, as remarked above, lies chiefly in their facilitation of the speedy exchange of new information. Almost from the first they have done this by the publication of scientific papers in their own journals, as well as by arranging lectures and meetings. Today, when scientific work may be pursued along similar lines in many different parts of the world, opportunities for personal contact at lectures and meetings are necessarily insufficient, and the journals published by the scientific societies are correspondingly important. Increasing specialization has brought into existence scores of new scientific societies, studying such specialized branches of science as microbiology, biochemistry, geophysics, and so on. Many of these societies have members in all parts of the world, and though their occasional meetings and lectures are very valuable their main value lies in their journals and other publications, through which all the members can be kept informed of the work being done by their colleagues.

Those scientific societies which have been able to acquire permanent premises have also served a most useful purpose by building up libraries. In them they have gathered together not only complete sets of their own publications but also of those contemporary journals and books which are of value to their members. The libraries of the scientific societies, particularly of those which have been long established, are therefore invaluable to the student. Several of the older societies are also custodians of many articles of historic interest. Besides contemporary portraits of their more distinguished members they often possess manuscripts, apparatus, and personal belongings of the great scientists of the past. Such heirlooms have more than a merely antiquarian interest, for they serve to arouse and nourish the sense of dignity and continuity so essential to the maintenance of high endeavour.

While scientific societies played an important part in the early development of science, today they have become entirely indispensable channels for the dissemination and recording of new knowledge. In common with other learned institutions, many are now encountering financial and other difficulties both in carrying on their existing services and in making the improvements demanded by the present rapid development of science. It should be their policy to maintain a lively and progressive attitude and to discover and fulfil the contemporary requirements of their members. In return it is clearly the duty of scientists to afford the societies not merely financial but also active personal support.

Editor: E. J. HOLMYARD, M.A., M.Sc., D.Litt., F.R.I.C.
Deputy Editor: TREVOR I. WILLIAMS, B.A., B.Sc., D.Phil.
Foreign Editor: J. A. WILCKEN, B.Sc., Ph.D.

Imperial Chemical Industries, Nobel House, Buckingham Gate, London, S.W.1.

Atomic energy—threat and promise

R. E. PEIERLS

The physical facts upon which the deliberate release of atomic energy is based are now generally familiar. In the present article, Professor Peierls discusses the potentialities of atomic power, particularly for peaceful uses. He argues that all the applications hitherto suggested amount really to doing better, or more cheaply, things that can also be done by other means. Entirely novel applications of atomic energy will doubtless be discovered when the world has grown more used to the immensely powerful tool now at its disposal.

INTRODUCTION

In public discussion of the prospects of atomic energy, the threat to the future of civilization which the atomic bomb represents tends to overshadow the promise of benefits from the constructive applications of atomic power. After the first public announcements on the bomb, exaggerated claims for the possibilities of an impending 'atomic age' appeared, particularly in the popular press, and the reaction to them discredited the whole subject.

Serious thought about the prospects is, in any case, made difficult by the lack of information, due partly to secrecy restrictions and partly to real uncertainties in the physical, chemical, and engineering data.

In the present article I shall endeavour to appraise the positive possibilities as they appear today, and as far as this is possible within the limits of available information. In many instances it will not be possible to give definite answers, but merely to indicate the factors on which the answers depend and the types of problems that have to be solved before the answers can be found.

It does not seem necessary to summarize the physical facts on which atomic energy is based, since by now a number of simple introductions are available (see page 57).

THE ATOMIC BOMB

In discussing the potentialities of atomic energy it would be futile to ignore atomic weapons, not only because they were the first and, up to now, the only important practical application, but because the threat which they represent must always override all imaginable advantages. If there is to be another world war fought with atomic weapons and, as we have to expect, with other new weapons of mass destruction, prospects are so grim that the constructive applications of atomic energy would give us poor comfort. If, on the other hand, international politics were to progress to a point where we felt reasonably confident that there would not be another major war, this would represent such an enormous step forward that the direct benefits would for a long time appear insignificant in comparison.

This problem is essentially political and outside the scope of this article, but it may be appropriate to summarize here the features of the atomic bomb that make it play such an outstanding part. We have often been reminded that the atomic bomb raids were not the most destructive single operations in the past war, nor the ones involving the greatest number of casualties. The essential new feature lies in the comparative cheapness of these weapons, once the necessary scientific and development work has been done, and in their small bulk, which makes it possible to deliver them by a variety of means against which an effective defence and even an adequate warning system seem quite impossible. As a result of this, once stocks of atomic bombs are available, surprise action becomes much easier than with other forms of attack, which require large operational forces.

It is probably not true that atomic bombs in themselves would make a future war much more destructive. Other destructive techniques were perfected during the recent war, and there is no doubt that such weapons as rockets of the V_2 type were only just beginning to play their part. Other new developments, like chemical and biological warfare, about which very little has been said in public, share many of the features of atomic bombs. Attention has focused on the atomic bomb because its effect has been demonstrated.

One of the essential features of atomic warfare is that it is bound to result in heavy damage and casualties to all parties (assuming that both sides possess these weapons) and that, while it may be possible to deliver a crippling blow in a very short time, this will not prevent retaliation striking even

the country whose stocks of atomic bombs are superior. Hand in hand with that goes the fact that, while they could destroy a country, atomic bombs could not be used to occupy and hold it. Hence they lend themselves to irresponsible destructive action but not to any calculated aggressive war that is likely to benefit the aggressor.

It is important to stress this feature because it indicates that the destructive nature of atomic weapons may itself be of ultimate benefit if it helps to bring home to everyone the lesson that the use of military force for aggression does not pay.

CONSTRUCTIVE USES OF ATOMIC BOMBS

Supposing the threat of atomic warfare could be eliminated, are there any other uses to which atomic bombs could be put? No definite suggestion has so far been made that can bear examination, but the problem is so new that the possibility should not be ruled out altogether. The use for mining and other similar engineering operations would seem extremely difficult, for three reasons. One is the enormous intensity of the blast action in the immediate neighbourhood of the explosion centre, which leads to a much more thorough destruction than is necessary or desirable. This immediately rules out the use in all those mining operations where one is dealing with a narrow vein of ores. One would probably then find the ores thoroughly mixed up with the surrounding matter, and their recovery would be more difficult than before.

The second difficulty lies in the fact that it is very difficult to use atomic explosions in a controlled way and to limit their effects, since in any use underground the range of the blasting action will depend greatly on the nature of the geological structures, which are hard to explore over a region as large as the likely range of the explosion. In addition, the power of atomic bombs is not exactly predictable and will vary somewhat from one instance to another, depending in most types of design on whether or not a stray neutron happens to initiate a chain reaction before the mechanical assembly of the components is complete. Even if the power of the explosion could be made precisely reproducible there would still remain the difficulty that the precise range in different types of rock or soil could be ascertained only by experimentation (as it is with ordinary mining explosives), and such experimentation covering the necessary variety of conditions would be a prohibitive task.

The third difficulty is that in an underground explosion the greater part of the fission products, with their intense radioactivity, would probably remain on or below the ground and that therefore the affected area would become inaccessible for a very long period. This difficulty did not arise in the past because, for explosions in air, most of the radioactivity is carried up into the upper atmosphere, while in underwater explosions it is reduced fairly rapidly by dilution.

In spite of these difficulties, one could imagine cases in which it is not necessary to limit the range precisely. This applies, for example, to breaking a gap in a mountain range so as to alter the course of a river, or to breaking up an ice-pack that threatens to cause serious obstruction. The danger of radioactivity may not be serious where speedy access to the area is not needed or where one can make sure that rising air will disperse the products.

ATOMIC POWER

Leaving aside the very speculative possibility of utilizing atomic explosions, we are left with atomic chain reactions conducted in a controlled way. Their most obvious use lies in the power they generate. From the point of view of basic physics this problem is completely solved, and there is no difficulty in operating an atomic pile in such a way as to generate heat at whatever rate it can be removed from the pile by a suitable cooling medium. Considerable engineering problems remain, however, of which the most serious is the question of reaching a temperature at which the generation of power becomes economical.

The chief reason for this difficulty is that in all piles constructed with ordinary uranium the reproduction factor, i.e. the number of secondary neutrons available to cause further fission for each primary neutron resulting from the previous fission process, is only slightly larger than unity. The chain reaction can, of course, proceed only if this reproduction factor exceeds unity, and any cause that will reduce it by more than the slight available margin will prevent the pile from operating. Such a cause is represented by the absorption of neutrons in impurities, in the cooling medium, or in materials introduced for structural reasons. Hence if we think of piles made of uranium metal and graphite, like the piles now operating at Hanford in North America, we must not only use uranium and graphite of an extremely high degree of purity, with tolerances for certain impurities of the order of a few parts in a million or better, but the amount of water or other cooling medium used in the pile and the

amount of other materials introduced for structural purposes or for preventing corrosion of the uranium metal must be extremely limited. Because of such limitations the Hanford piles do not permit a temperature-rise that would allow the generation of steam at even a modest pressure. There seems no doubt, however, that a determined attack on the remaining engineering problems will lead to a solution in which the temperature of the pile can be raised considerably. As far as the basic nature of the reaction is concerned, there is no practical limitation to the temperature. There is, in principle, no reason why it should not be taken up to a point where the utilization of the heat by means of steam engines or turbines or any other methods of generating mechanical energy is most favourable. How far this can be carried in practice is as yet unknown, and the higher the temperature the greater the difficulties in protecting the structural components against corrosion or against mechanical distortion. Both problems are accentuated by the presence of intense radiation, which accelerates chemical action because of the high degree of ionization and dislocation of atomic structures that it causes, and which may even reduce mechanical strength.

Some of the problems in the way of high-power piles would be eased if the piles were constructed not of ordinary uranium but of enriched material, obtained either by separation of isotopes or as a result of nuclear transformations carried on in piles of the Hanford type or in the power piles themselves. In this case the active content of the piles is increased, and with it the margin in the reproduction factor. Piles constructed in this way have much more latitude in the use of structural materials and cooling medium, but the corrosion problems remain, and at the same time the piles burn a very much more expensive fuel.

Another difficulty in the operation of all piles is represented by the dangerous radiations, contributed in about equal parts by the neutrons themselves and by the gamma rays resulting from neutron-capture in the pile and from the radioactive fission products. This necessitates heavy protective shields around the piles, and arrangements for doing any adjustments on them by remote control. It also requires arrangements to prevent the escape of radioactive materials by way of the cooling medium into the machinery driven by the pile. Otherwise this machinery would become radioactive and would have to operate inside the radiation shield; it could then not be serviced except by remote control.

Similarly, refuelling of the pile and removal and treatment of depleted fuel have to be carried out by remote control. These obstacles have been overcome in the piles now in operation, but they represent severe limitations in the engineering design.

ADVANTAGES OF ATOMIC POWER

We have seen that, even if not all engineering problems in the way of the production of atomic power have been solved, they at least appear soluble. What will be gained by making atomic power available on a large scale? We shall first consider large stationary power units, used to generate electricity.

The cost of electricity from such stations will depend on the cost of the fuel, the capital charges and running expenses of the pile itself and its auxiliaries, and the cost of generating machinery and distribution. The last item is much the same as for conventional power stations, except that the factors governing the location of atomic power stations are different; this may affect the distribution cost. The pile itself probably represents a much greater capital investment than a boiler plant, though not necessarily a higher running cost. The actual cost is hard to estimate when the design is as yet unknown. Since the pure materials (uranium, graphite, etc.) required for the pile represent a major item, the cost must also depend on the scale on which these are being manufactured, and hence on the overall scale of the atomic power programme.

The cost of the raw material at pre-war market prices is very small compared to that of a corresponding amount of coal. No doubt the applications of atomic energy make uranium a more valuable material, and indeed, because of its military importance, there is presumably no free market for it at all. Even so, quite a considerable rise in the cost of raw material would hardly affect the cost of electricity from such a plant.

These considerations show that, since at present the generating and distribution costs are a large item in the price of electricity, the cost of atomic power is likely to be about the same as for electricity from coal and that, even if we assume the pile to cost no more than a boiler plant and the fuel to cost nothing, the price of electricity would fall by only some 20 or 30 per cent.

A recent official statement by the American authorities confirms these rough estimates, and arrives at a price for electricity that is slightly higher than the current one. A slight increase in the cost of coal at the power station would

equalize the difference. No details were quoted, but it seems likely that a similar estimate for conditions in Great Britain would show a slight balance in favour of atomic power. These figures are not meant to be precise, and further experience may well show a somewhat greater margin on either side.

It follows that we can hardly expect a revolutionary change in the price of electricity. One specific advantage of atomic power is the small bulk of the fuel consumed, which makes the power stations independent of access to railways and waterways. This allows the planning of power stations close to the consumer, and reduces the difficulties of distribution; it also gives more freedom in placing the stations in positions where the low-grade heat that is always a by-product of the generation of power can be used for heating or for industrial purposes.

This specific advantage is of outstanding importance in the case of countries, such as Italy, in which there are no adequate resources of power and where the transportation of coal becomes an important factor. It may even make possible new projects, such as the irrigation of desert areas in which the supply of power would today present prohibitive difficulties.

In addition, atomic power may add to our resources if and when the depletion of known coal deposits, or lack of people who are attracted to mining as a career, limits the supply of coal. At equal cost, it would surely be preferable to employ fewer men in coal mines. It should not be assumed, however, that atomic power stations may in the immediate future reduce the demand for coal. Even disregarding the time still needed for the necessary development work, it will take a long time to build atomic power stations on a sufficient scale to have any effect on world economy. It will take an even longer time to convert to electricity such things as railways, domestic fires, and so on, the conversion of which would become worth while only if the price of coal were to increase relatively to that of electricity. In any case it must, of course, be remembered that there will always remain some need for coal for metallurgical, chemical, and other purposes.

All these considerations are based on the assumption that sufficient amounts of atomic fuel can be found. The next section will deal with the question of their availability.

SUPPLY OF RAW MATERIALS

From the previous section it is clear that the availability of atomic fuel is a vital question for the success of any atomic power project. It would seem an easy task to estimate the accessible deposits of suitable ores and compare them with the expected demand, but there are a number of factors complicating this issue. Firstly, the only large atomic piles that have so far been operated work with ordinary uranium. Since the major constituent of this is uranium 238, which does not undergo fission with the slow neutrons on which these piles operate, it is only the rare constituent uranium 235 which is consumed in this operation. This represents only 0·7 per cent. of the uranium found in nature. In the course of this operation, however, some of the neutrons are captured in uranium 238 and convert it (through the intermediate nucleus, neptunium 239) into plutonium 239. It is well known that this conversion was, in fact, the main object of the Hanford piles. It has been stated that the number ν of secondary neutrons obtained from each fission process is greater than one (otherwise no chain reaction would be possible) but less than three. Of these ν secondary neutrons from each fission, one must in a steady chain reaction be captured in another fissile nucleus so as to maintain the chain reaction, and the remainder $(\nu - 1)$ will either escape from the surface of the pile or be absorbed in one or the other of its constituents. Escape from the surface can be made small by increasing the size of the pile, but there are unavoidable losses due to absorption in the 'moderator,' i.e. the substance used for slowing down neutrons (which in the Hanford piles is graphite), in the cooling medium, and in the necessary structural elements of the pile. The remainder may be available for absorption in uranium 238 or in other suitable materials mixed into the pile for this purpose. This number is less than $\nu - 1$, and from the published figures is therefore certainly less than two. We thus know with certainty that at most two atoms of plutonium will be made for every atom of 235 burned in the pile, and it is also clear that this is a generous upper limit.

If it were possible to run the pile in such a way that this number were greater than one, the amount of plutonium generated would be greater than the amount of 235 burnt up. If the properties of plutonium were similar to those of 235, this would mean that by leaving in the pile an appropriate fraction of the plutonium so made we could in this way make up for the uranium 235 that was burnt, and such a pile could therefore continue operating until the depletion of

uranium 238 reduced the rate of production of plutonium. In these conditions it would therefore be possible to burn not only the uranium 235 but a substantial fraction of the uranium 238.

With our assumptions, the condition for this process is that $\nu - 1$ should exceed one, i.e. that ν should exceed two. There is no guidance from published figures as to whether or not this is the case. Actually we have made the assumption that plutonium is about as efficient a fuel as uranium 235; if it differs appreciably, the critical limit for ν may be somewhat different from two. It will, in any case, be increased by the unavoidable loss of neutrons through absorption in other parts of the pile.

Since, as this process continues, we shall be burning plutonium rather than uranium 235, its success will also depend on the value of ν for the fission of plutonium.

Lastly, it is known that a new fissile material can be made by the bombardment of thorium with neutrons, and that this new material, which is an isotope of uranium of weight 233, may also be suitable for a chain reaction. No evidence is available on the merits of this isotope as an atomic fuel compared with uranium 235 or plutonium, or on the number of neutrons emitted in its fission.

It is, of course, conceivable that there may be similar processes as yet undiscovered starting from other raw materials, but this does not appear very probable.

All the above uncertainties in the data make the position about raw materials quite obscure. If it should turn out that in a pile starting with ordinary uranium the plutonium produced will more than offset the consumption of uranium 235, and also that as the pile turns over to consuming plutonium the amount of plutonium produced is greater than that consumed, it will be possible to utilize most of the atoms of ordinary uranium. On the other hand, if this is not possible the material will become almost useless when a substantial fraction of the 235 has been burnt. There is, therefore, an uncertainty of about a factor 100 in the amount of uranium required to maintain a given power output. Alternatively, the reaction can be conducted in such a way that some of the excess neutrons are not absorbed in uranium 238 but in thorium, and if it should turn out that the production of 233 more than offsets the initial consumption of 235 or plutonium and later on the consumption of 233, when this becomes the major fuel in the pile, it may be possible to run the power stations in a way in which ultimately the fuel is only thorium without a continuing consumption of uranium. This would at once add substantially to the supply of raw materials upon which we can draw.

Quite apart from this uncertainty, the amount of uranium that we can expect to be available is hard to estimate. There are at present only a few known deposits containing uranium ore in sufficient concentration to make its extraction profitable, but, even if further surveys should not lead to the discovery of new important deposits, it is well to remember that uranium is a common element contained in many minerals (such as ordinary granite) in very low concentration. No methods have as yet been worked out that would make the extraction of uranium from such poor ores a feasible operation. The concentration of uranium in some poor ores is, however, larger than, for example, the concentration of gold in most ores that are commercially worked for gold, and it is possible that a chemical process could be found which would effectively make this uranium available. This would open up sufficient quantities of uranium for any power programme that is likely to be needed in the foreseeable future.

Evidently the question whether any particular extraction process will make low-grade ores economically interesting depends on the price at which the fuel would make the production of atomic power compete successfully with those from other fuels. At present the price of the raw uranium is quite a small fraction of the estimated cost of atomic power, and a considerable increase in the cost of mining and extraction could be tolerated without altering the picture substantially. The limit depends on the place in which power plants are contemplated, because of the cost of transportation of coal, and on the likelihood of an increase in the price of coal owing to the exhaustion of suitable deposits, and other factors.

We must conclude that, while the uncertainty in all these facts certainly does not allow us at this stage to feel assured that a sufficient supply of atomic fuel can be obtained, it is equally impossible at present to exclude this possibility. It is certainly of sufficient promise to justify intensive study and development work.

MOBILE POWER AND OTHER SPECIFIC APPLICATIONS

Can atomic piles be made suitable for small units to be used in ships, trains, etc.? There are a number of factors which make the operation of small plants uneconomical. The first is the

critical size. It is known that for each reacting system there is a least size at which chain reaction becomes possible, since for any system of smaller size the number of neutrons lost by leakage from the surface reduces the reproduction factor below the critical limit. In the ordinary pile made of uranium metal and graphite we have already seen that the margin in the reproduction factor is very small. Hence only a small leakage of neutrons can be tolerated, and the least size of plant becomes very substantial. If one desires a power unit with a small power output, the plant will still have to be at least of the critical size and will therefore be very bulky. In addition, the amount of atomic fuel locked up in such a power unit is then very substantial, and the unit therefore represents a relatively large capital investment.

Things are more favourable if one can use concentrated atomic fuel, i.e. either uranium 235 obtained from a separation plant, or plutonium, or possibly uranium 233 from thorium. In the case of these substances the reproduction factor is considerably larger, and this brings the critical size down to quite a convenient magnitude. In fact, it is likely that in practice the size of such a unit would be determined by the requirement of getting in the necessary amount of internal surfaces for heat-extraction purposes. On the other hand, such concentrated fuels are very much more expensive. In the case of uranium 235 this would have to be produced by an isotope separation plant of the type of the plants that produced the material for one variety of atomic bomb, although the degree of separation need not be the same as that suitable for the bomb. Plutonium and uranium 233 are produced in piles, and their cost depends essentially on the considerations referred to in the previous section. If it turns out that a suitable pile can not only regenerate the fissile material necessary to keep the pile in operation, but also leaves something to spare, it might be comparatively easy to get fissile materials as by-products of power production.

Even for piles with enriched fuel, however, there remains the need for protective shielding, and it has been estimated that the minimum weight of such a shield is about a hundred tons. This clearly at once rules out use in cars or trains, but a weight of this order is quite modest if one thinks of its use, for example, in a large ship. In fact, it would appear possible in the case of a ship to use the surrounding water as part of the shield and thereby further reduce the deadweight that has to be carried. Whether atomic ships are a practicable proposition is therefore merely an economic question. In comparing the cost of atomic power with coal or oil one has to bear in mind that ships would have to use concentrated atomic fuel, as it does not seem likely that a power unit of the size, say, of the Hanford piles would be suitable for a ship. It is impossible to estimate at the moment the cost of the concentrated fuel. On the other hand, it is certainly an advantage that the weight of the fuel consumed during the voyage would be quite negligible, and this factor would be particularly important for long journeys without refuelling.

As regards aeroplanes, the need for a heavy shield is certainly a most serious handicap, and atomic planes cannot be practical unless one increases by a large factor the overall size of the plane and, with it, the size of the runways, etc. Even if one is prepared to do this, one would probably not want to operate the power unit of a plane on low-grade heat, which would necessitate the use of steam engines. The solution of this problem is therefore dependent on raising the temperature in the pile to a level where more modern forms of conversion to mechanical power become possible.

On the other hand, the low weight of the consumed fuel is in this case a most important consideration, and if an atomic plane is possible at all it will have a practically unlimited range without reduction of the carrying capacity.

A particularly interesting problem is that of using atomic energy in rockets for interplanetary travel. If one looks at this problem purely from the point of view of the balance of energy, it is clear that atomic power overcomes the major handicap of other such rockets. The energy necessary to carry a certain amount of ordinary fuel beyond the range of attraction of the earth is greater than the energy obtained by burning the fuel, whereas for atomic fuel it forms a negligible fraction. However, rockets operate on the recoil produced by ejecting the combustion products backwards, and, since the mass of the combustion product is negligible in the case of atomic power, such rockets would have to carry material specially for the purpose of ejecting it. Thereby one loses all the advantage of the low fuel weight, unless it is possible to eject materials at a speed in excess of that of the combustion products in ordinary material. This means that one would have to use atomic power for heating a suitable substance to a temperature higher than the flame temperature in ordinary rockets. Though there is

nothing to prevent this in the basic process of a chain reaction, the engineering difficulties are clearly formidable.

RADIOACTIVE ELEMENTS

To return from speculation to well-established fact, we next consider the uses of radioactive elements produced in piles, either as fission fragments or by the neutron bombardment of almost any substance. These can be used for most of the purposes for which naturally radioactive elements have been used in the past, such as medical therapy and industrial radiology, but they are becoming available in practically unlimited amounts, and with a much greater variety of properties. A doctor can, for example, choose for his treatment a radioactive element of a suitable lifetime and can thus inject it close to the affected spot. The decay of the activity will then limit the total dose. At the same time there is more freedom in the choice of the hardness of the radiation. By choosing a radioactive isotope of a suitable element it may be possible to cause the radioactivity to accumulate in a suitable place in the human body, and this principle has been successfully applied in the United States to the treatment of a rare form of thyroid disease by means of radioactive iodine.

In radiology, gamma rays may for certain purposes be preferable to X-rays because of their greater penetrating power, and because they allow the use of a very compact source which may, for example, be placed inside a small opening insufficient to house an X-ray tube. Atomic piles can produce such sources with intensities greatly in excess of those practicable with radium.

A much more important application, however, lies in the use of radioactive tracers for chemical or biological research. This gives the possibility of labelling certain atoms and recognizing them afterwards, while allowing them to take part in a chemical or biological process in which their history will be precisely the same as that of other atoms of the same element. This allows us to recognize, for example, the exchange of two atoms of the same element between two different molecules, and it allows us to identify the origin of substances in a living body—to see, for example, whether they are taken up as part of the current food intake, or whether they come from deposits of the same substance in other parts of the body. Such tracer methods were already being employed before the war, using radioactive isotopes made in the laboratory by means of cyclotrons or other machines. Atomic piles provide both greater quantities and greater variety.

A further advantage of such tracers is that their radioactivity may make it possible to observe them in the living body, while keeping the intensity of radiation well below the safe tolerance limit. It is immediately evident that this method of studying chemical reactions in the living body is an extremely powerful tool.

Similarly, there are applications of such tracer elements in other fields, notably in engineering research. These possibilities have not yet been adequately explored.

The amounts required for such experiments are usually quite small, so that a pile which, as a power station, has a very modest output can keep a number of laboratories supplied. In the United States such radioactive tracers are already freely available, but their export is prohibited by Act of Congress. In England work is in hand on the construction of a pile for this purpose.

OTHER POSSIBILITIES

All the applications discussed above amount really to doing better, or more cheaply, or more conveniently, things that could also be done by other means. Nobody has so far shown enough foresight to say what completely new uses may be found for atomic energy. Similar reasoning applied to the steam engine or to electricity or to the internal combustion engine, when they were first introduced, would evidently have given a very incomplete picture of their promise. It may well be that the really important applications will not be thought of until the world has got more used to the new possibilities.

However that may be, I hope to have made it clear in this necessarily vague and incomplete report that a great wealth of new possibilities is opened up by atomic power, and that, if we show enough enterprise and determination in exploring them, they are bound to add materially to the resources of the world.

REFERENCES

SMYTH, H. D. *Atomic Energy for Military Purposes* (reprinted by H.M. Stationery Office).

Statements Relating to the Atomic Bomb (H.M. Stationery Office).

Atomic Survey (published by the Atomic Scientists' Association).

VOLKOFF, G. M., and WALLACE, P. R. *Atomic Energy* (published by the Canadian Association of Scientific Workers).

Penguin Science News, II (February 1947).

NIMMO, R. R. *Atomic Energy* (Pilot Press, 1947).

The Royal Botanic Gardens, Kew

SIR EDWARD SALISBURY

'Kew Gardens' are famous the world over: to the layman as one of the sights of London, and to the botanist, horticulturist, and arboriculturist as their own particular Mecca. The four main divisions of the institution, namely the living collections, the herbarium, the museums, and the research laboratory, together form an unrivalled instrument for the recording and expansion of our knowledge of plants and plant products. Sir Edward Salisbury, the present Director, describes the Gardens and their main service to the study of vegetable life.

The Royal Botanic Gardens at Kew are an institution that, in a typically English way, had its origin in private enterprise. The initiative dates back to some 180 years ago, when Princess Augusta (mother of George III) began to form a botanical collection which the acumen of Sir Joseph Banks quickly raised to the first rank of importance. Even so, the collections declined in the early years of the nineteenth century and might have been lost as a national asset had it not been for the report of Lindley, the first Quain Professor of Botany at University College, London. Now, more than a century later, another Quain Professor has become Director. The Gardens as we see them at the present day owe much of their planned beauty to the first two directors, Sir William and Sir Joseph Hooker. The Hookers were followed in turn by Sir William Thiselton Dyer, Sir David Prain, and Sir Arthur Hill, each of whom effected further improvements.

The extent of the Gardens today is some three hundred acres—a far larger area than the original garden—and it is because a second garden was joined to the first that the plural still persists in the official title. Many of our countrymen in Britain are rightly proud of Kew, but its real value is probably more appreciated, and for better reasons, by our kith and kin overseas than by those at home. The latter too often regard Kew as an especially attractive public park, and though its value as a summer resort amid floral beauties must not be underrated, yet the wider recognition that this aspect is but a by-product of its real function might perhaps induce a greater and more intelligent regard for the specimens it contains.

The number of living species which are here cultivated is quite remarkable, and it is a tribute alike to the horticultural skill of the garden staff and to the adaptability of the plants themselves that even in the open there are to be seen many thousands of species culled from the most diverse regions and soils. In the Temperate House, probably the largest glasshouse in the world, over an eighth of a mile in length, are to be seen the Acacias and Epacrids of Australia and New Zealand; the Camellias of Japan; a wonderful display of Tree Ferns, Rhododendrons from the Himalayas and Java; the marvellous pink blossoms of *Magnolia mollicomata*; and the flamboyant blooms of Tibouchina from tropical America. Or we may walk over to Decimus Burton's masterpiece, the great Palm House, so well proportioned that its great size—more than 360 ft. long and 66 ft. high—is but half realized. Here a collection of Cycadaceae gives us some faint idea of what the vegetation of the earth must have looked like in Jurassic times, when plants of this affinity were an important feature not only in the tropics but elsewhere.

Here too we see the Screw Pines, and tall Palms striving to push through the roof. Or again we go to the Tropical Fern House and see Giant Ferns on the one hand and on the other the puny modern descendants of the giant Lycopods that formed so marked a feature of Coal Measure forests. Then, having thus paid tribute to the outmoded fashions of plant life that achieved their zenith in former epochs, we wander out into the Arboretum, where thousands of species of dicotyledonous and coniferous trees represent the dominant types of the arboreal vegetation of the present day.

All these collections of living plants, comprising more than forty thousand species grouped to please as well as to enlighten, are but a part of the mechanism that Kew provides for the accurate naming of plants and the growth of knowledge of the vegetable kingdom. Indeed, the living collections form a supplement to the Herbarium housed in the extensive buildings to the north of the main entrance, where more than five million specimens are preserved—a vast collection in which the

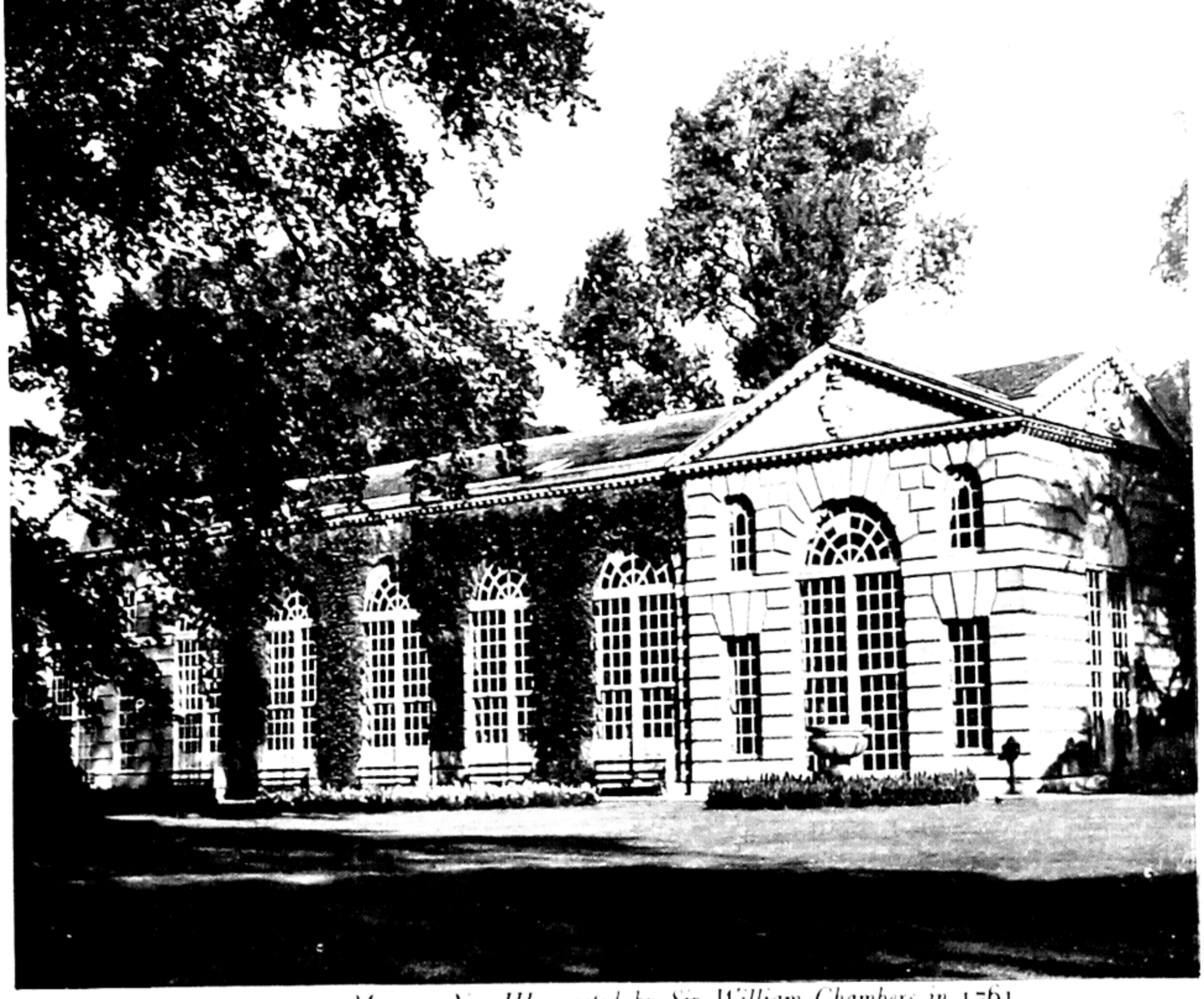


FIGURE 1 – *Museum No. III, erected by Sir William Chambers in* 1761.



FIGURE 2 – *The Pagoda, a relic of the Oriental phase* (1761).



FIGURE 3 – *A glimpse of the Cycad collection in the Palm House*





FIGURE 4 (*above*) – *Rhododendrons and tulips in the Broad W*

FIGURE 5 (*left*) – *Part of the Rock Garden.*



FIGURE 6 – *The Palm House, Decimus Burton's masterpiece, erected* 1844–8.

proportion of types, co-types, and paratypes is incomparably high. For this reason the Kew Herbarium far surpasses in importance any other collection of such a cosmopolitan character in the world. Hence it is that Kew is the taxonomist's Mecca, and systematic botanists from all over the world are, in normal times, to be found carrying out research within its walls. Naturally, the Kew collections are especially rich in types from the British Empire, and Kew has thus been the source of production of a long series of Floras, from the famous *Flora Antarctica* and the Flora of British India, published between 1872 and 1897, which treated of some 14,000 species, to the Flora of tropical West Africa, which appeared just before the recent war. Here too is produced the *Index Kewensis*, in which are enumerated the Latin binomials of all flowering plants, with references to the source of the original description. Every five years a supplement is issued to include all newly described plants in this category. The whole constitutes an indispensable tool for all botanical taxonomists. Much of the knowledge and experience of Kew in respect to the taxonomy of particular regions is embodied in the series of floras already referred to, and in numerous monographs of particular families or genera. The Herbarium with its large library is in fact an extensive taxonomical research institute, where a permanent staff and visiting scientists are continually advancing our knowledge of the world's flora.

The *Kew Bulletin of Miscellaneous Information* is the means of recording much of the more-specialized research that is carried on at Kew alike in the fields of pure taxonomy, plant morphology and anatomy, economic botany, and botanical exploration, and it is a matter for concern that the destruction of the stocks of this periodical by enemy action precludes our meeting the numerous demands for copies that we have received from all over the world.

In the Jodrell Laboratory, research work of an experimental character is carried on, and this laboratory is also the department of the gardens concerned with anatomical investigation. Here has been produced a new taxonomic account of the anatomy of dicotyledonous plants, to be published by the Oxford University Press in the near future. This will embody the information contained in the English edition of Solereder, in preparing which Dr Boodle (late Keeper of the Jodrell Laboratory) played so large a part, together with the mass of information accumulated during the past forty years. It was in this laboratory that the classical physiological experiments of Brown and Escombe were carried out, that D. H. Scott did most of his work on fossil plants, and that during the war the possibilities of rubber production from the dandelion (*Taraxacum kok-saghys*) in English conditions were assayed. Here, too, methods of propagation by growth-promoting substances and taxonomic cytology have been studied. Like the Herbarium, it furnishes accommodation for visiting scientists working on the plant material Kew can so richly provide.

Four museums of Economic Botany in different parts of the Gardens house the extensive collections of plant products. They provide not only an indispensable means of reference for the multitudinous inquiries that come in from all parts of the globe, but act as a valuable source of research material. The vast collection of fibres, timbers, drugs, and food products, both in the raw state and in manufactured form, is here to be found arranged on a taxonomic basis.

Thus the four major divisions of the organization of the Institution, namely the Herbarium, the living collections, the Museums, and the Jodrell Laboratory together constitute a powerful instrument for research and information concerning the identity and characteristics of plants and their products.

But while the living collections are of first importance as a supplement to the *hortus siccus*, they play, and indeed have long played, a most important role as a source for the distribution of economic species throughout the Empire. The part which Kew played in the initiation of plantation rubber and the cinchona industry is too well known to need reiteration. Kew was also responsible for the dissemination of cocoa and oil palm to West Africa, of pineapple to a number of areas, of the nut *Macadamia ternifolia* to Hawaii, and more recently of the oil-producing tree Aleurites to various Dominions and Colonies. These are but a few examples of the extensive plant distribution which has been rendered possible by the skilled use of the Wardian case. In connection with banana-research in the West Indies, Kew functioned not only as a distributing agency but also as a quarantine station. This latter aspect has gained added emphasis with the increased importance of virus diseases, for unless plants carried from one part of the world to another are healthy their distribution may be a menace rather than a service.

The vast numbers of visitors to Kew every year are a testimony to its great popularity as a resort,

and though for many the Gardens are but a beautiful amenity, they provide for many others a permanent horticultural display where newly introduced or rare species can be seen by the botanical student, the research worker, and the professional or amateur grower. The three stout volumes of *Trees and Shrubs Hardy in the British Isles* by W. J. Bean, a former Curator at Kew, is a gardening classic that embodies much of the cultural lore that has been accumulated during the passage of years. Another such is *The Botanical Magazine*, which was started by William Curtis,[1] but for more than a century has been edited at Kew and contains coloured illustrations and descriptions of new or noteworthy species. It will be realized that the cultural experience of more than a hundred years which has been amassed at Kew enables it to serve as an unusually well-equipped training-ground for horticulturists, and many former Kew students now occupy positions of importance the world over. Moreover, the wide range of material which the gardens can furnish is constantly drawn upon for research in many fields of scientific activity.

Almost every post brings requests for such material. It may be to test the active principle of some plant alkaloid, to investigate the chromosome number of a suspected polyploid, or to compare the epidermal characters of a living Cycad with those of a Jurassic prototype. It is needless to say that, owing to limitations of space and staff, Kew cannot attempt to supply educational material in the broader sense, but in so far as its resources are required for genuine research these are placed freely at the disposal of investigators in universities and other recognized institutions of higher learning—as far as is consistent with the proper maintenance of the collections. The intercourse with overseas botanists is now a highly prized tradition, and it is pleasant to record that though wartime conditions diminished this activity they never caused it to cease, and that it is already being resumed.

The original Botanic Garden was only about nine acres in extent and remained little more until shortly after 1840, when, during the first directorship under Sir William Hooker, most of the present land was added. The only substantial extension since that period was the area of thirty-seven acres presented by Queen Victoria. This comprises the Queen's Cottage grounds, which, as they were left with the proviso that they should remain more or less in a wild state, cannot be appropriately used for planting other than native species.

The area thus acquired a century ago seemed ample—hence the lavish expenditure of space on multiplication of the same species in avenues and in other ways. Since that time the vast influx of species, from both the Old World and the New, has, especially so far as trees are concerned, strained the limits of Kew severely, and at the present time an appreciably larger area would be more than welcome, whilst the glasshouses are now far from adequate.

The Palm House took four years to construct and was completed in 1848. The Temperate House was erected some ten years later and, like most of the glasshouses at Kew, is now too small to meet present needs, despite the fact that it occupies about three-quarters of an acre. Both these houses suffered from enemy action during the late war, a large proportion of the glass of the Temperate House being broken when a heavy bomb exploded in the fork of a near-by beech tree. It is a tribute to both the skill and the devotion of the staff that the resultant losses in plants were much smaller than expected. The Orchid Houses, enriched by gifts from the collection of Sir J. Colman, now contain a remarkable collection of orchid species. The remaining houses contain collections of economic species of tropical and temperate ferns and insectivorous plants, whilst for the general public the *Victoria regia* House, where this giant annual species flourishes, is perhaps the greatest attraction after the conservatory devoted to decorative plants.

Out of doors, the 'order beds' provide valuable material for students, while most of the shrubby and arboreal species are also grouped taxonomically. A recent departure from this tradition has been made, in the interests both of efficient culture and of educational value, by the establishment of a chalk garden.

The different parts of Kew exhibit a variety of styles in landscape gardening, but fortunately, as befits a botanical garden especially, the English style, which we owe in considerable degree to the influence of Kent, Sir W. Chambers, and Pope, who lived at Twickenham, is that which preponderates. Thus so far as conditions permit the ideal aimed at is the display of the natural growth and habit of the species concerned, and indeed the motto of Kew might well be 'Science and Beauty.'

[1] See ENDEAVOUR, Jan. 1946.

The Chemical Society (of London) after one hundred years

C. S. GIBSON

As the oldest society of its kind in the world, The Chemical Society (of London) will find no one to quarrel with its proud assumption of the title 'The Chemical Society' *tout court*. For over a hundred years its Officers and Fellows have blazed new trails in the advancement of chemical knowledge, the reputation of the Society ranking second to none among chemists the world over. This year the Society officially celebrates its centenary—the celebrations should have been held in 1941, but were postponed owing to the war. We congratulate the Society on this happy and auspicious occasion, and wish it a long-continued vigorous life.

In 1938 H.M. King George VI became Patron of The Chemical Society (of London), and the Council began to take steps for the celebration of the centenary of the Society in 1941 by appointing Organization and Executive Committees. At the Ninety-eighth Annual Meeting in 1939, Sir Robert Robinson, F.(now P.)R.S., Waynflete Professor in the University of Oxford, became President, and it was hoped that he would preside over the Centenary Celebrations to be held in April 1941, which were to be followed immediately by the Eleventh International Congress of Chemistry.

Such arrangements as had been made by September 1939 had to be put on one side, and, for example, the formation of an Advisory Chemical Research Council was deemed to be far more important in the national interest than any further immediate consideration of arrangements for the celebration of the centenary of even the oldest chemical society in the world.[1] Sir Robert Robinson was, indeed, the President at the Hundredth Annual Meeting in direct line of succession to Thomas Graham, F.R.S., President in 1841. In the Centenary Presidential Address, Sir Robert Robinson, after recalling some of the earliest details of the Society and the ever-to-be-remembered services to chemical science rendered by Thomas Graham and Robert Warington, the first Honorary Secretary, as the real founders of The Chemical Society,[2] made the following statement:

> The present is no time for festive occasions, for reunions with our distinguished Honorary Fellows, for international intellectual co-operation generally, and certainly not for an organized scientific congress. Therefore the Council has decided to postpone our Centenary Celebrations, which must be compounded of all these elements after the war. This decision has no negative qualities but is a positive affirmation of our intention to organize as soon as possible an occasion worthy of the Society's splendid record and high position among the academies of the world.

Professor J. C. Philip, F.R.S. (Honorary Secretary 1913–24, Councillor for nine years, Chairman of the Bureau of Chemical Abstracts for the first nine years, 1923–32), succeeded Sir Robert Robinson as President. Few have served the Society more faithfully and efficiently than Professor Philip, and his death after only four months as President was a severe loss. He had undertaken the writing of the Centenary History of the Society; this will be completed by Professor T. S. Moore, who, as Honorary Secretary and Chairman of the Publication Committee, has already placed the Society greatly in his debt. As President, Professor Philip was succeeded by Dr W. H. Mills, F.R.S. (Cambridge). It fell to the next President, Professor W. N. Haworth, F.R.S. and Nobel Laureate (Birmingham), to

[1] Justus von Liebig's personal inspiration played a substantial part in the founding of The Chemical Society; and it is significant that the German Chemical Society was founded in 1866, the year after the return to Germany of A. W. von Hofmann, F.R.S. (President, 1861–3) from this country. The Chemical Societies in other countries were founded as follows: France (1857), Russia (1868), America (1876).

[2] The Society was formally constituted as 'The Chemical Society of London' on 30th March, 1841. The designation was changed to 'The Chemical Society' when the Royal Charter was granted in 1848. Nevertheless, according to the records, the Jubilee of 'The Chemical Society of London' was celebrated on 24–25th February, 1891, under the Presidency of Dr W. J. Russell, F.R.S. Among the names of those present at the Jubilee Banquet is that of Mr W. P. Wynne. Happily, Professor W. P. Wynne, F.R.S., is still a Fellow of the Society, to which he has rendered most notable service as Honorary Secretary, Editor, Councillor, and President (1923–5).

lead the Society through the last year of the war period and for one year during the aftermath. Professor (now Sir Norman) Haworth, with his Honorary Officers and Council, although occupied with many difficult problems confronting the Society, began at once to continue the preparations for the celebration of the Centenary, which he announced would be held in London in July 1947, and would be followed there by the Eleventh International Congress of Chemistry.

The celebration of the Centenary of the Society thus falls in the second year of office of the present and fifty-sixth President, Professor C. N. Hinshelwood, F.R.S., Dr Lee's Professor of Chemistry in the University of Oxford. Sir Robert Robinson became President of the Royal Society in November 1945, and is, after Sir William Crookes, O.M., D.Sc., F.R.S. (President 1887–9), the second Past-President of The Chemical Society to assume the most important office in British science.

The Chemical Society was inaugurated in the rooms of the Royal Society of Arts, and for nearly eight years continued its meetings there. After the Society had been granted its Royal Charter the Council decided that the possession of its own rooms would be more in keeping with its newly acquired dignity. From then until 1857 the Society had its rooms at various addresses, at none of which did it remain as long as at the Royal Society of Arts. There are indications that The Chemical Society in those days quickly ceased to be popular with its landlords, because the Fellows making communications persisted in carrying out experiments, frequently attended by the emission of divers odours, in inadequately ventilated rooms. In 1857 The Chemical Society, with the help of the Royal Society, was allotted by the Government a meeting-room and a library room (furnished by the private subscription of the Fellows) in Old Burlington House. The present apartments in (New) Burlington House, built by the Government to accommodate the Royal Academy, the Royal Society, and certain chartered scientific societies, were allotted to The Chemical Society in 1873–4. This accommodation has not been extended for more than seventy years.

The Fellows of The Chemical Society are proud of their home—it houses so many treasures, busts, medals, and pictures illustrative of progress in chemistry and of chemists in many parts of the world. At the same time they have recognized its painful inadequacy for many years. The Library and its annexe on the top floor have had to be modified to provide for the largest chemical library in Britain. In 1873–4 the library consisted of some three thousand volumes, whereas new accommodation has had to be contrived for some fifty thousand volumes. Every room in the building with the exception of the meeting-room —and that may have to be pressed into service— has had to be fitted with shelves and racks, and in some places the latter are so close together that it is difficult to move between them. Literally every inch of space is used for the continually growing collection of books and periodicals. Part of the Society's collection of its own periodicals is stored in various places outside. The accommodation may have been adequate for the 733 Fellows in 1874, but the membership is now over seven thousand, and the Library is also used by members of other societies.

On the first floor is the meeting-room, which accommodates 157 persons. As one may suspect, it is often totally inadequate for the meetings of The Chemical Society and of other societies which have met there for many years. The room has a certain dignity. Behind the demonstration table is the presidential chair, bearing the arms of the Society. On the wall above the presidential chair is the unique painting of Thomas Graham, the honoured first President.[1] On the walls are portraits of all the past Presidents, but unfortunately there is now insufficient space for them to be displayed worthily.

When the Society is in session, the mace is placed before the President or his deputy. The mace was presented to the Society in 1930 by Mr A. H. Hooker. After their election, Fellows are formally admitted at all Ordinary Scientific Meetings and sign the Obligation Book, which contains the signatures of all formally admitted Fellows since the foundation of the Society. The earliest signatures are those of Robert Warington and Thomas Graham.

By the entrance to the meeting-room is the 1914–18 War Memorial to Lt.-Col. E. F. Harrison, C.M.G., and to the twenty-nine other Fellows who died on service. Col. Harrison rendered conspicuous service to the nation by his intense, self-sacrificing energy and his wonderful success in equipping the troops with protection against

[1] This portrait was painted in 1931 from a daguerreotype (in the possession of Dr Alexander Scott, F.R.S., President 1915–17). The artist (Mr W. A. Budd) experienced no difficulty in depicting faithfully the features of Graham; he was, however, anxious to have a model for the rest of the picture. Professor G. A. R. Kon, F.R.S., was the suitably dressed model.

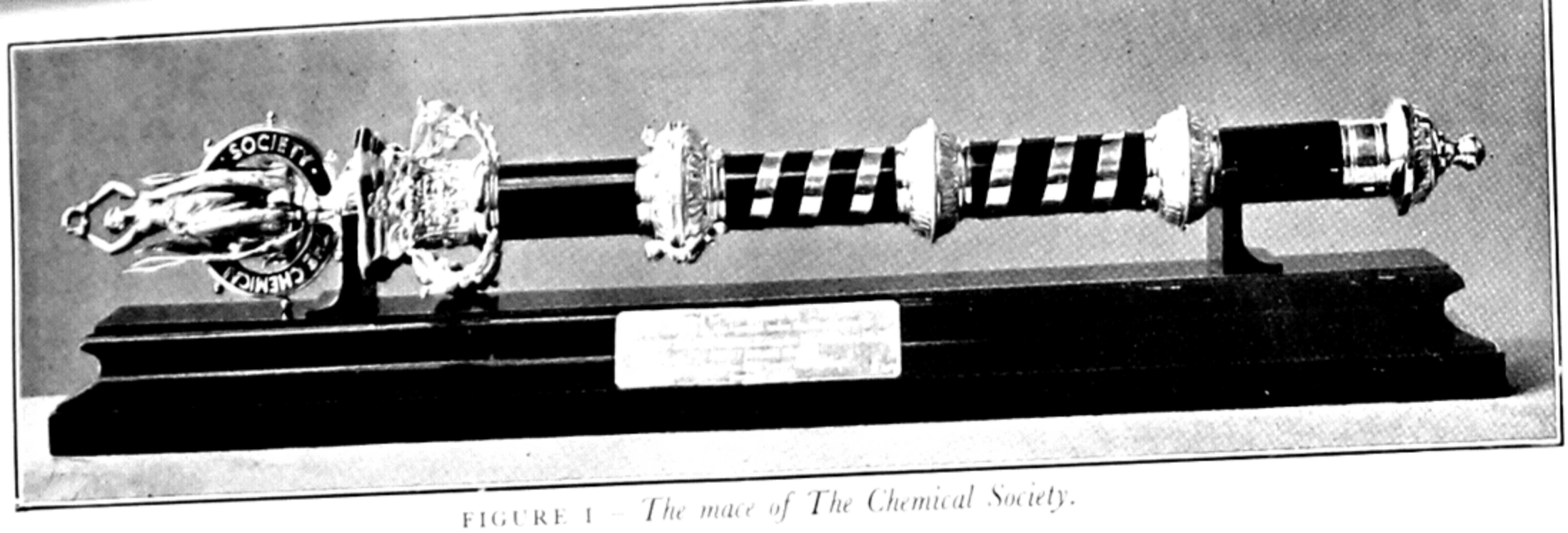


FIGURE 1 – *The mace of The Chemical Society.*



FIGURE 2 – *Professor W. H. Perkin, M.A., Sc.D., LL.D., F.R.S. President* 1913–15.

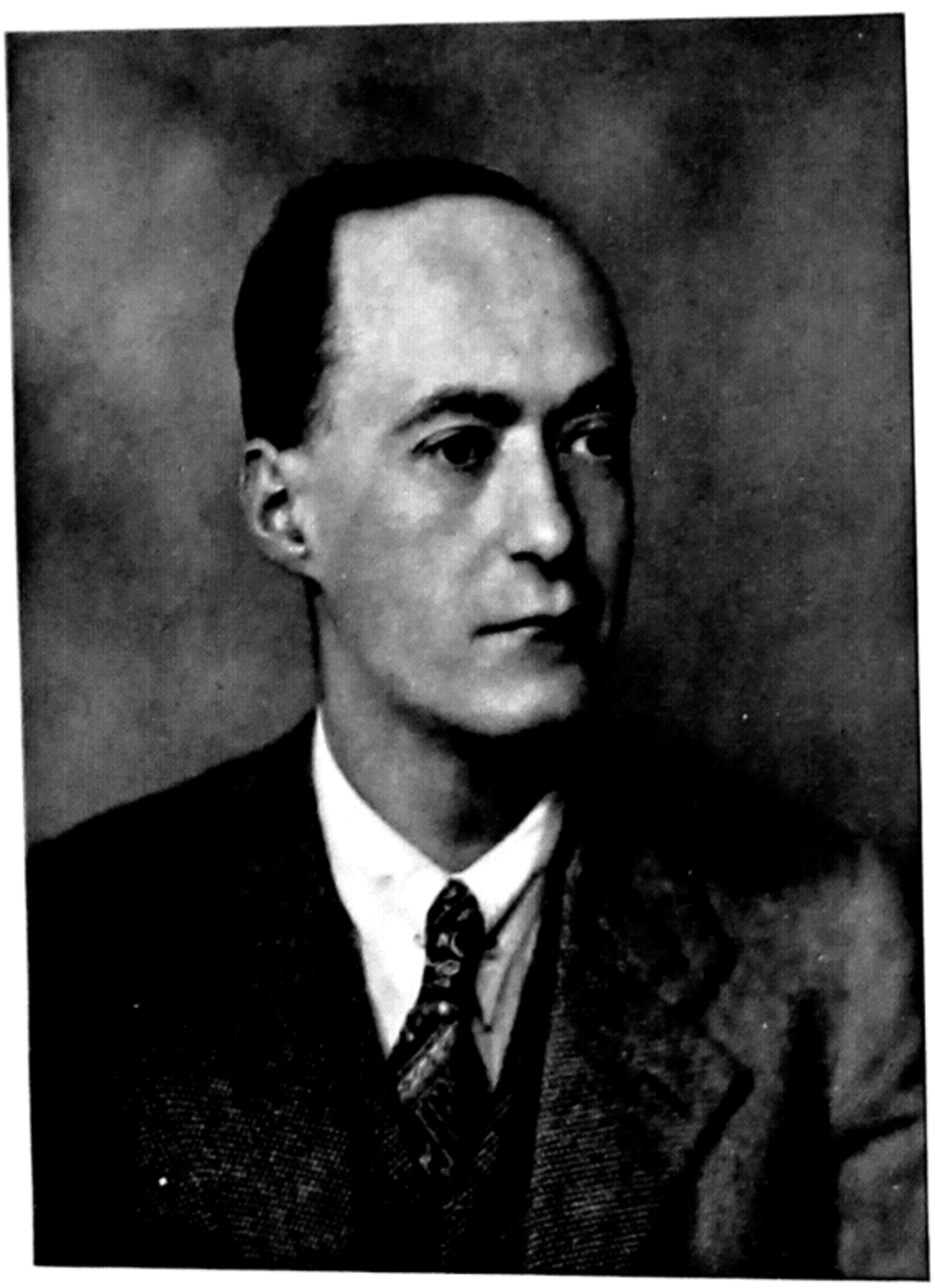


FIGURE 3 – *Professor C. N. Hinshelwood, M.A., Sc.D., F.R.S. President* 1946–



FIGURE 4 – *Professor Sir Robert Robinson, M.A., D.Sc., LL.D., P.R.S. President* 1939–41.

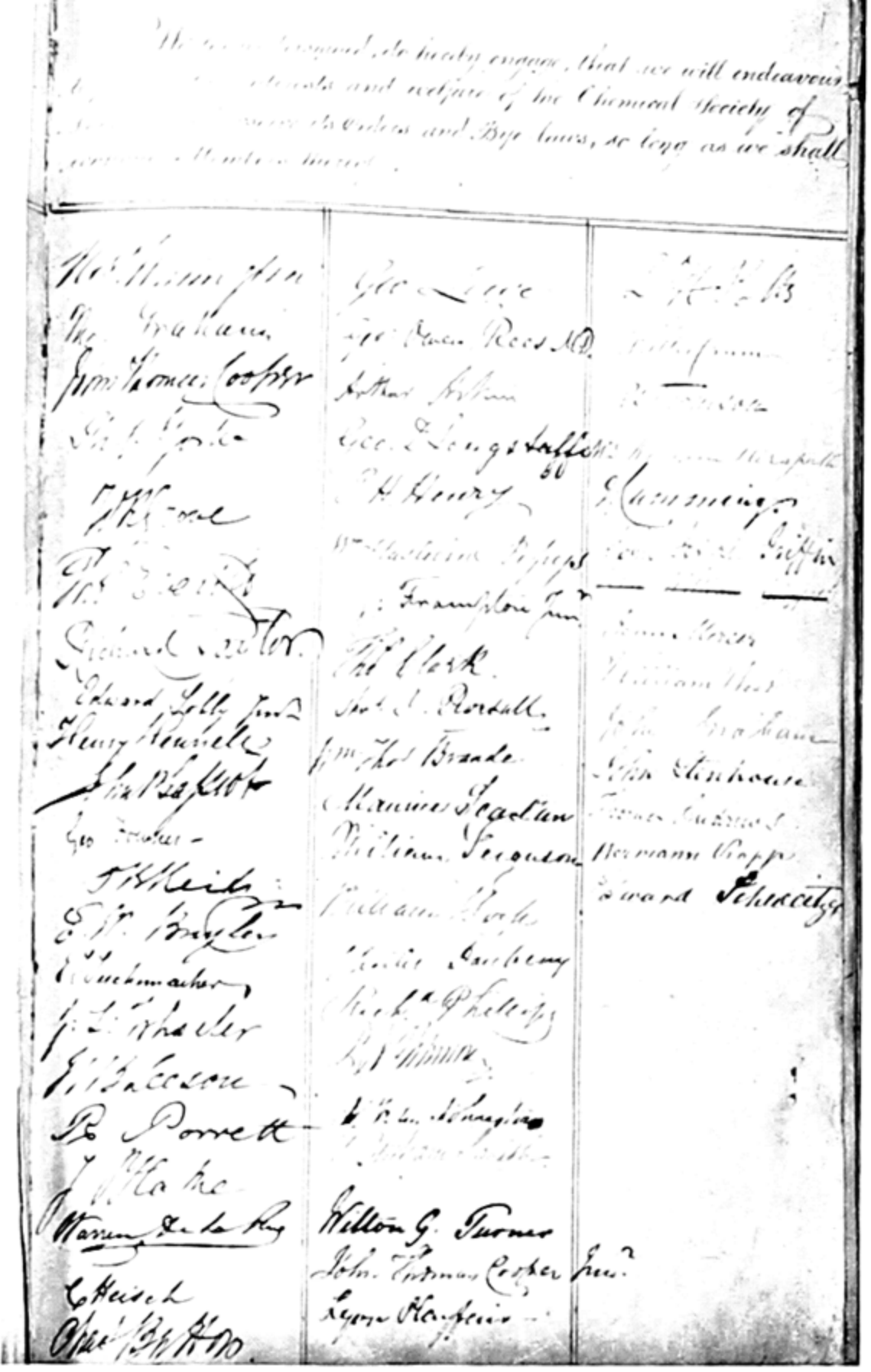


FIGURE 5 – *The first page of the Obligation Book, bearing as its first signatures the names of Robert Warington and Thomas Graham.*

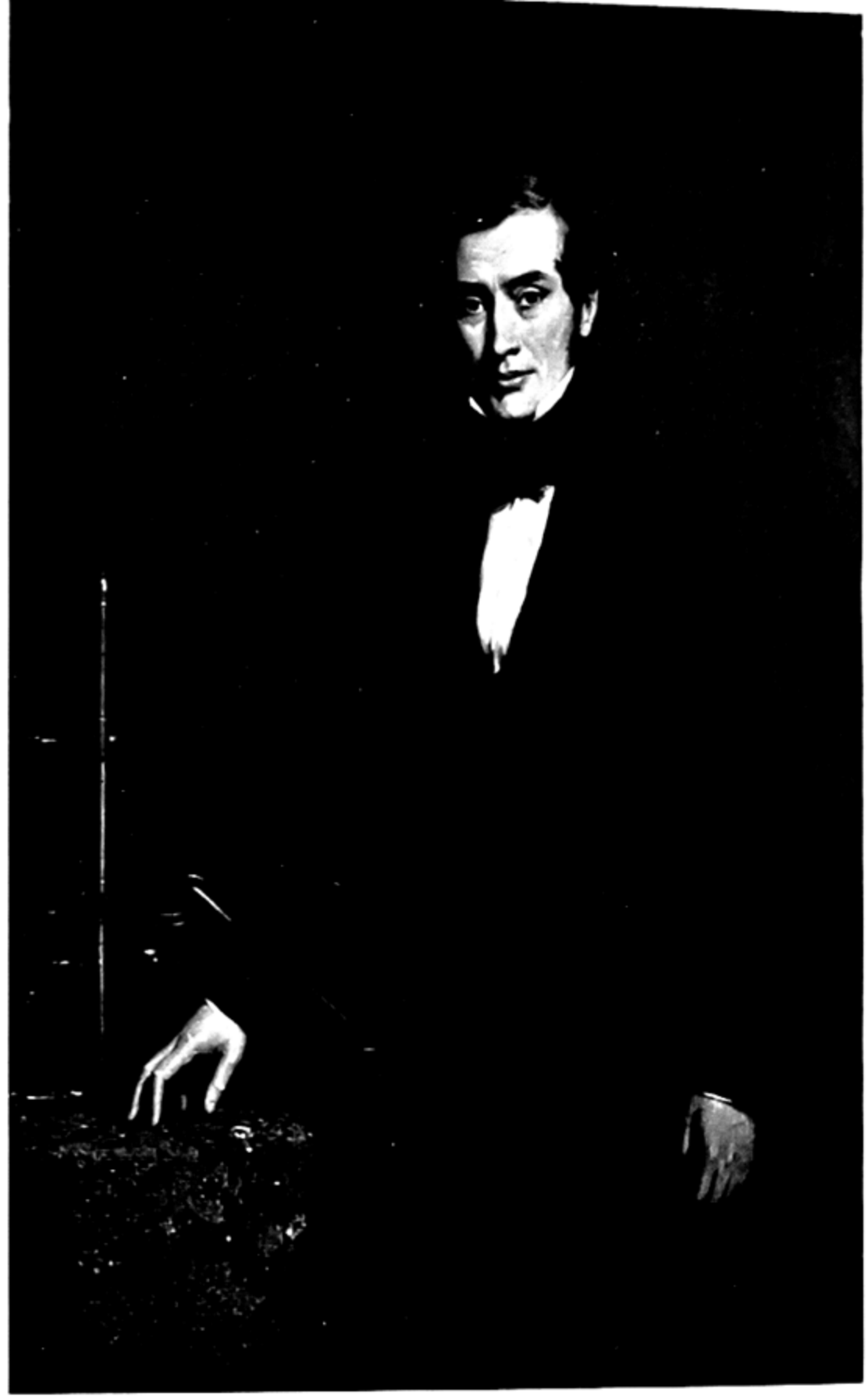


FIGURE 6 – *Thomas Graham, M.A., D.C.L., F.R.S. President* 1841–3, 1845–7. *(By courtesy of the Science Museum.)*

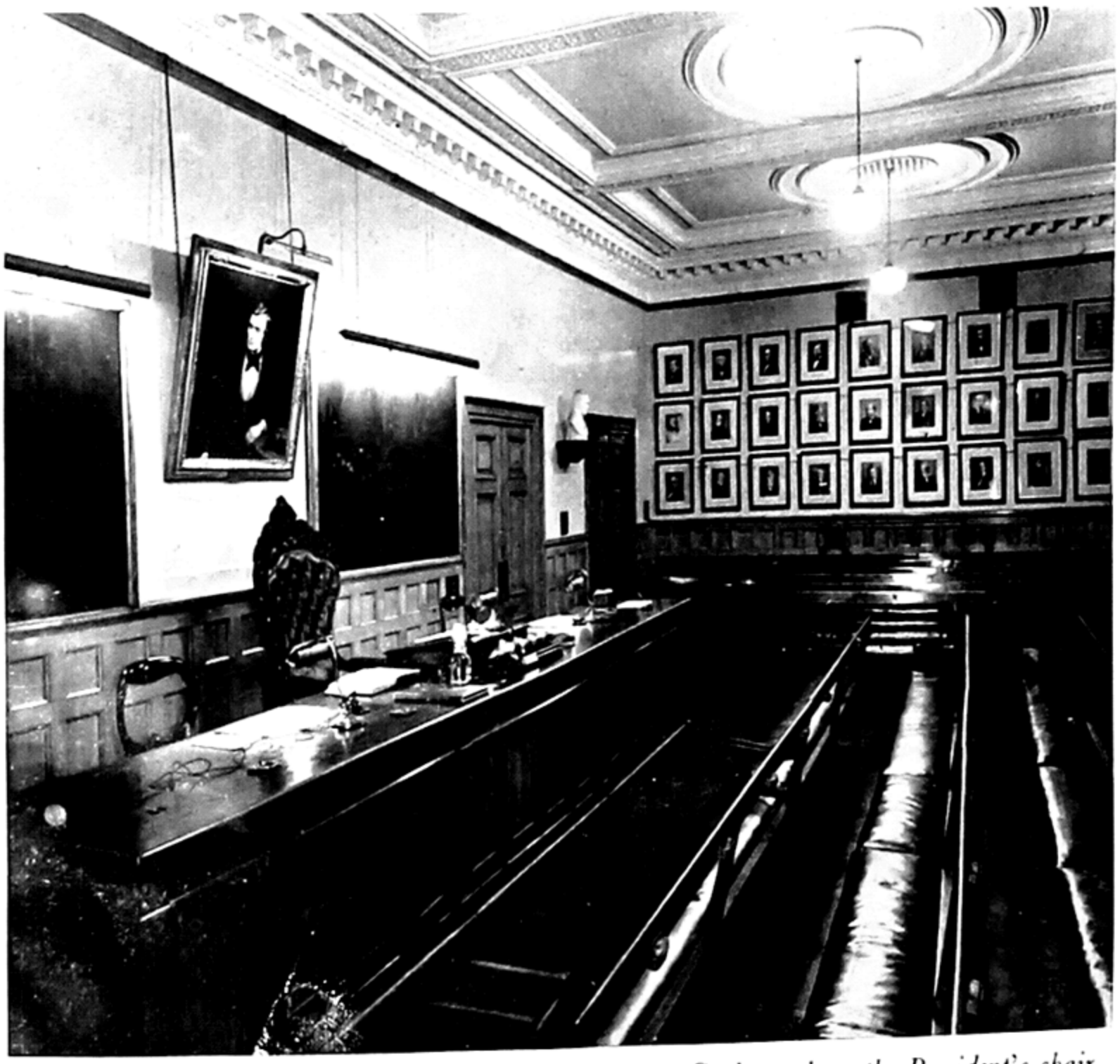


FIGURE 7 – *The lecture room, with portrait of Thomas Graham above the President's chair.*

poison gas. The cost of this memorial was defrayed from a privately subscribed fund of which part was used as a trust to establish the Harrison Memorial Prize of the value of £150. This is awarded every three years on the recommendation of a Committee composed of the Presidents of the Chemical Society, the Society of Chemical Industry, the Pharmaceutical Society, and the Royal Institute of Chemistry to the chemist, man or woman, not over thirty years of age, who shall have made the most meritorious contribution to chemical science during the previous five years. The first award was made in 1924 to Dr C. R. Harington, F.R.S.

The General Secretary's room was formerly the laboratory. On the ground floor are the rooms for the Honorary Officers and for Council Meetings. Apart from their use as part of the Library, these rooms, like the meeting-room, are used for office and editorial purposes whenever they can be spared. This very brief description hardly does justice to the home of The Chemical Society, which by the success of the work the Society has accomplished for the science has now become far too small.

Special lectures have been a feature of the proceedings of the Society since its inauguration. The Faraday Lectureship (1868), and the more recently endowed Hugo Müller, Pedler, and Liversidge Lectureships held by distinguished British and foreign chemists, provide valuable accounts of the most important developments in chemical science during the last eighty years.

In 1920 women were admitted to the Fellowship on the same terms as men. This change, somewhat heatedly contested, was followed by increasing the facilities to Fellows not resident in London. Regional representation of Fellows on the Council was instituted, alternate Annual Meetings are held outside London, and special and endowed lectures are delivered in provincial centres. Local representatives keep the Fellows in their respective districts informed of the Society's activities, and co-operate with other chemical organizations in the holding of joint meetings, discussions, and lectures.

From its foundation the Society has concerned itself with the publication not only of its own original contributions and lectures in its world-famous *Transactions* or *Journal*, but of abstracts of papers appearing in other journals. At first only British journals were abstracted, but in 1871 the abstracting service was extended, and from 1873 the abstracts were separated from what up to 1925 were styled *Transactions* and then became the *Journal*. In 1882 the Society of Chemical Industry began the publication of Abstracts of Applied Chemistry Papers. In 1923 the Bureau of Chemical Abstracts was started as a joint committee of The Chemical Society and the Society of Chemical Industry, concerned with the publication of *Abstracts A* (Pure Chemistry) and *Abstracts B* (Applied Chemistry). This first essay in co-operation between chemical societies has been an unqualified success. The pioneer work in the formation of the Bureau was carried out by Professor J. C. Philip, F.R.S., the first Chairman. The present Chairman is Dr L. H. Lampitt, President of the Society of Chemical Industry and *ex officio* member of the Council of the Chemical Society. It is now the Bureau of Abstracts, and is supported by The Chemical Society, the Society of Chemical Industry, the Physiological Society, the Biochemical Society, the Anatomical Society, and the Society for Experimental Biology. It is the largest and most important scientific abstracting organization in Britain.

The Society has published *Annual Reports on the Progress of Chemistry* since 1904, and can be justifiably proud of their success and high reputation among chemical publications. Publication of these Reports has been uninterrupted even during the two world wars, and important extension by the additional publication of review articles is now fully planned.

Co-operation between societies and organizations interested in the progress of the various branches of chemistry has been prominent, especially since the end of the 1914–18 war. In this movement The Chemical Society has always taken a prominent share. Even before the formation of the Bureau, The Chemical Society made its valuable library available to members of other societies. This co-operation of The Chemical Society with the Society of Chemical Industry and the Royal Institute of Chemistry has been greatly advanced by the establishment in 1935 of the Chemical Council. This consists of twenty members representing the three societies and the Association of British Chemical Manufacturers, which has helped The Chemical Society financially and in other ways for many years. Professor E. K. Rideal is the Chairman, and Mr F. P. Dunn, Hon. Treasurer of The Chemical Society since 1938, to whom The Chemical Society owes so much, has placed the Society further in his debt by acting as Vice-Chairman of the Chemical Council.

Each constituent of the Chemical Council

retains its own individuality. It has established a Joint Library Committee with eight contributing organizations. Under the Chairmanship of Mr Dunn it has effected economies and increased efficiency in the production and distribution of the publications of The Chemical Society and the Society of Chemical Industry. Its system of joint membership of the three chartered organizations is in operation, and this has resulted in a marked increase in the Fellowship of The Chemical Society.

Since 1919 the establishment of Chemistry House, in which The Chemical Society will have an honoured place, has been the object of many efforts. The fulfilment of this project has now been assumed by the Chemical Council. If the Chemical Council is as successful in this as it has been and is in its other work—and there have already been generous benefactors—then The Chemical Society and its library will have in a reasonable time the accommodation they have so greatly needed and deserved for many years.

The Fellows of The Chemical Society can be rightly proud of the record of work accomplished by their Society for the extension of chemical knowledge during one hundred years, and of the Society's world-wide reputation. The future presents even greater opportunities than in the past for the work of the Society, and although they are conscious of many difficulties to be surmounted, its Fellows will by the quality of their investigations still further enhance its reputation.

PRESIDENTS OF THE CHEMICAL SOCIETY

	Years of Office
T. Graham	1841–1843, 1845–1847
A. Aikin	1843–1845
W. T. Brande	1847–1849
R. Phillips	1849–1851
C. G. B. Daubeny	1851–1853
P. J. Yorke	1853–1855
W. A. Miller	1855–1857, 1865–1867
L. Playfair	1857–1859
B. C. Brodie	1859–1861
A. W. von Hofmann	1861–1863
A. W. Williamson	1863–1865, 1869–1871
W. de la Rue	1867–1869, 1879–1880
E. Frankland	1871–1873
W. Odling	1873–1875
F. A. Abel	1875–1877
J. H. Gladstone	1877–1879
H. E. Roscoe	1880–1882
J. H. Gilbert	1882–1883
W. H. Perkin	1883–1885
H. Müller	1885–1887
W. Crookes	1887–1889
W. J. Russell	1889–1891
A. C. Brown	1891–1893
H. E. Armstrong	1893–1895
A. G. V. Harcourt	1895–1897
J. Dewar	1897–1899
E. Thorpe	1899–1901
J. E. Reynolds	1901–1903
W. A. Tilden	1903–1905
R. Meldola	1905–1907
W. Ramsay	1907–1909
H. B. Dixon	1909–1911
P. F. Frankland	1911–1913
W. H. Perkin (jun.)	1913–1915
A. Scott	1915–1917
W. J. Pope	1917–1919
J. J. Dobbie	1919–1921
J. Walker	1921–1923
W. P. Wynne	1923–1925
A. W. Crossley	1925–1926
H. B. Baker	1926–1928
J. F. Thorpe	1928–1930, 1930–1931
G. G. Henderson	1931–1933
G. T. Morgan	1933–1935
N. V. Sidgwick	1935–1937
F. G. Donnan	1937–1939
R. Robinson	1939–1941
J. C. Philip	1941–Aug. 1941
W. H. Mills	Aug. 1941–1944
W. N. Haworth	1944–1946
C. N. Hinshelwood	1946–

PAPER RESTRICTION

As a result of the shortage of power for industrial purposes in Great Britain, paper mills have been unable to maintain their normal production. A temporary reduction in the size of ENDEAVOUR will therefore have to be made, and each of the next two issues will consist of fewer pages than usual.

Some physical instruments used in medicine

DAVID S. EVANS

Chemistry has always found manifold applications in medicine, and was indeed, in the days of iatrochemistry, merely the physician's Abigail. At the present time chemotherapy basks in the glory of such discoveries as penicillin, the sulphonamide drugs, and paludrine. The applications of physics to medicine have so far lagged behind, except in such cases as the use of X-rays and radioactivity in diagnosis and treatment. The many recent advances, however, leave no doubt that physicotherapy has as bright a future as chemotherapy.

The use of X-rays and radioactivity in diagnosis and treatment represents one of the most striking ways in which medicine has made use of physical discovery. So successful indeed, have researches of this character become that an important feature of the relation between medicine and physics tends to be obscured. In spite of the tremendous successes of physics, and in spite of the valuable contributions which physics has made to medicine in the field of X-rays and radium, and in nerve physiology, the general contribution of physics to medicine is far smaller than it might be, and there are many valuable links between the two sciences waiting to be forged.

This is a surprising conclusion in view of the earlier history of the relations between them. Before the differentiation of the sciences, the links were close. Gilbert, the author of a famous treatise on magnetism, was Queen Elizabeth's physician; Copernicus was, at least ostensibly, a physician as well as a priest and an astronomer. Even much later, Thomas Young, known to physicists for his work on light waves, was a physician by training. von Helmholtz had his first education in medicine, and the early conclusions on the conservation of energy were based on physiological experiments.

It seems as if the division between the two sciences was a temporary one only, and now the gap is being closed. As medical men require for diagnosis a more and more detailed investigation of their patients it is inevitable that physical problems of diagnosis should come to occupy a larger place in their thoughts. As medicine arms itself with more and more complex instruments for diagnosis and treatment, so it meets more and more frequently physical problems of design beyond the capacity of the medical specialist to solve. Co-operation between the two sciences was greatly encouraged by the late war, when the medical profession found itself faced with problems of casualties and disease of an entirely new order of magnitude, and in the solution of some of them sought the aid of the physicist.

It is not unfruitful to begin the discussion with a consideration of the differences in viewpoint between the physicist and the medical man. On the one hand, the physicist is accustomed to the study of situations involving rather few variables: his experimental conditions are fairly accurately reproducible, and his interpretation of results has a mathematical exactness and niceness. If he is a mathematician as well, he will notice in himself a tendency to believe that he has said all that is worth saying about a problem once he has cast it into mathematical terms, and may even exhibit a dogged determination to defend his mathematical deductions as enshrining the whole truth.

The medical man, on the other hand, shares with his colleagues in the biological sciences all the difficulties consequent upon large individual variations in his material: his primary aim is to diagnose and cure, and here he is faced with a situation embodying an enormous number of factors which defy numerical definition. He tends, and rightly so, to rely on a general assessment of a complex picture in which many of the features have indefinite and almost imponderable qualities which can be judged only by experience.

This attitude indicates the medical problems which can be profitably studied by the physicist. He must, throughout, be guided by his medical colleagues and must not attempt to dominate the situation. The services which he can render are, firstly, to assist diagnosis by providing means for more accurate assessment of physical symptoms, so delineating more firmly part of the general clinical picture. Secondly, he can devote his

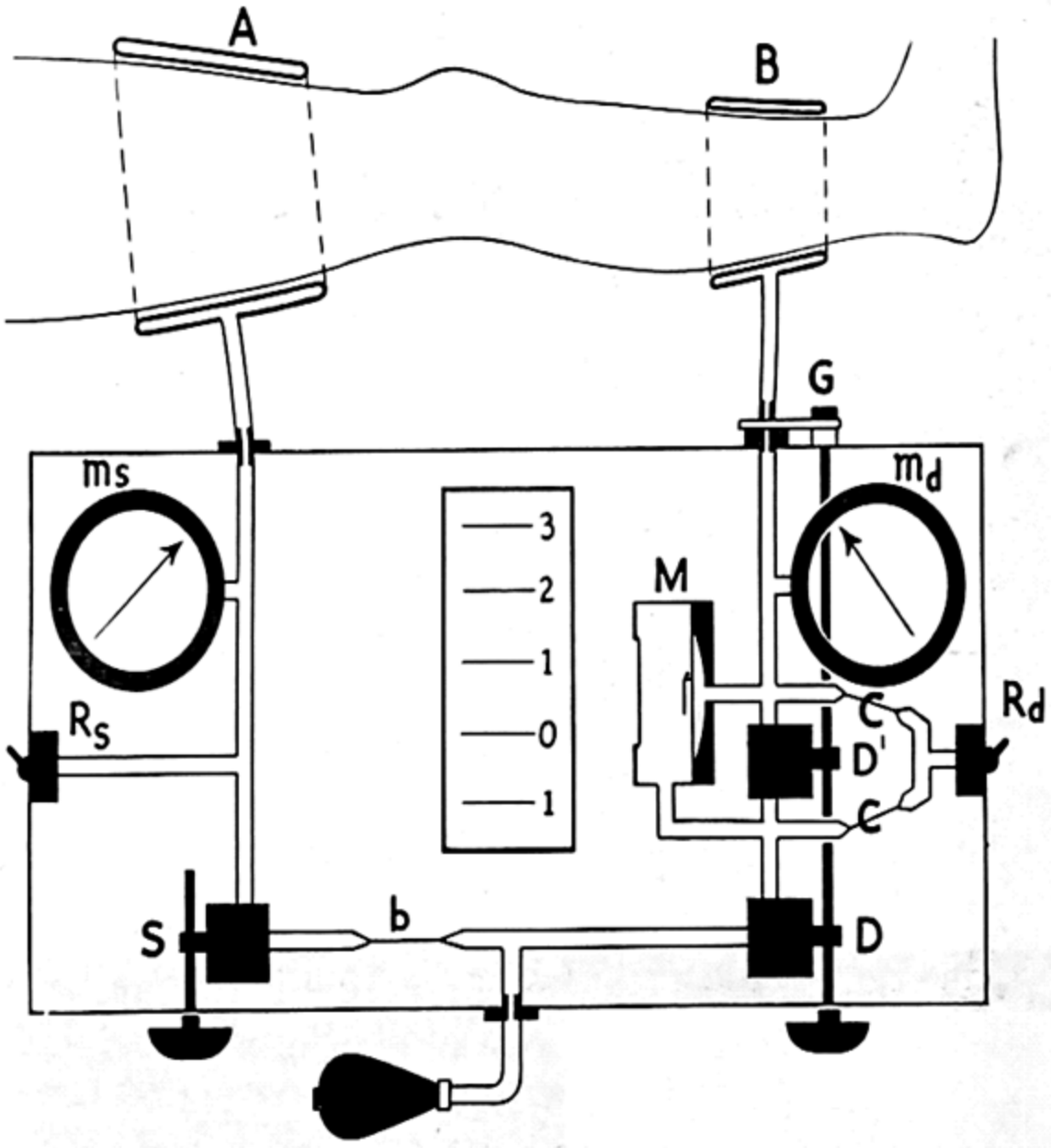


FIGURE 1 – *Circuit of blood-pressure indicator.*
(*Reproduced from the* British Journal of Anaesthesia.)

M = *Membrane manometer.*
m_s, m_d = *Aneroid manometer.*
D' = *By-pass tap.*
D = *Inflation tap, linked to* D′.
C–C = *Capillary.*
R_d, R_s = *Release valves.*
S = *Systolic circuit tap.*
b = *Capillary.*
G = *Safety gate.*

attention to methods of physical clinical treatment and, by physical investigation, render them more precise and more readily controllable.

A third feature of the relationship between the two sciences must be mentioned. As a result of his attempts to aid diagnosis the physicist may provide the medical man with some new instrument: this must be not only reliable in its readings but very robust and easy to operate. A device which is so delicate that it cannot withstand the hazards of use in general medical work, which often needs servicing, or which is so difficult to operate that the practitioner would be better occupied in giving his attention directly to the patient, will soon be discarded. Better by far to produce a less accurate device which can be operated by the turn of a switch and which will survive—for example in military use—a fall from a lorry [1].

Two examples of the work done by the writer in collaboration with Dr K. Mendelssohn will illustrate the practical application of these principles. The first problem was to devise an instrument for the measurement of blood-pressure, preferably by a continuous indication.

The medical background of this problem is as follows. A fall in blood-pressure is one of the earliest signs of the onset of shock in patients in the operating theatre. In casualties a low blood-pressure is a possible indication of a state of shock, although the difficulty here is that the normal blood-pressure even of healthy persons shows a wide variation. As an aid to the anaesthetist, however, who is responsible for keeping the patient in the operating theatre in good shape, the completest possible knowledge of the blood-pressure variations is of the first importance.

The pressure in an artery is not constant, but varies cyclically with the action of the heart. The standard medical method of specifying the blood-pressure is by the maximum and minimum pressures attained during each cycle, these being known as systolic and diastolic pressure respectively. The difference between the two is called the pulse pressure, and it is possible that this quantity represents the best index of the circulatory state of the patient.

The ordinary method of determining systolic and diastolic pressures is by the aid of a rubber cuff which is bound round the arm and can be inflated to any desired pressure, the pressure being read on a mercury or aneroid manometer. A stethoscope is applied to the brachial artery distal to the cuff, and the sounds heard in this at different cuff pressures form the basis of the estimation of the required pressures. Roughly the procedure is as follows. It is assumed that the pressure in the cuff is transmitted through the tissue to the artery. If, therefore, the cuff pressure be greater than systolic, the artery beneath the cuff will be occluded, no blood will flow past the obstruction, and no pulse sounds will be heard in the stethoscope. If the cuff pressure is lowered to a value intermediate

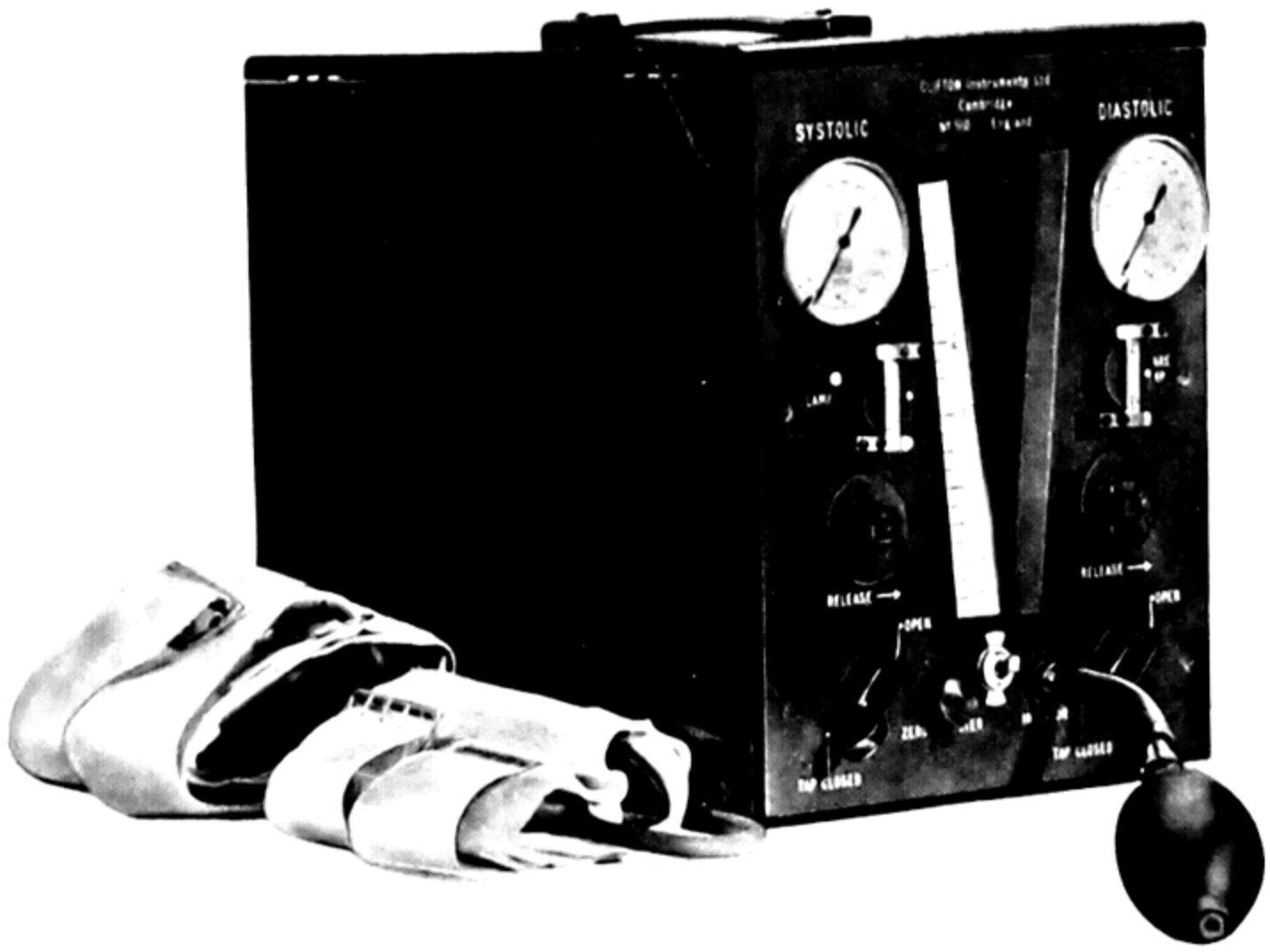


FIGURE 2 – *Blood-pressure indicator. The pulsations are shown by the movement of a light-spot on the central scale.*

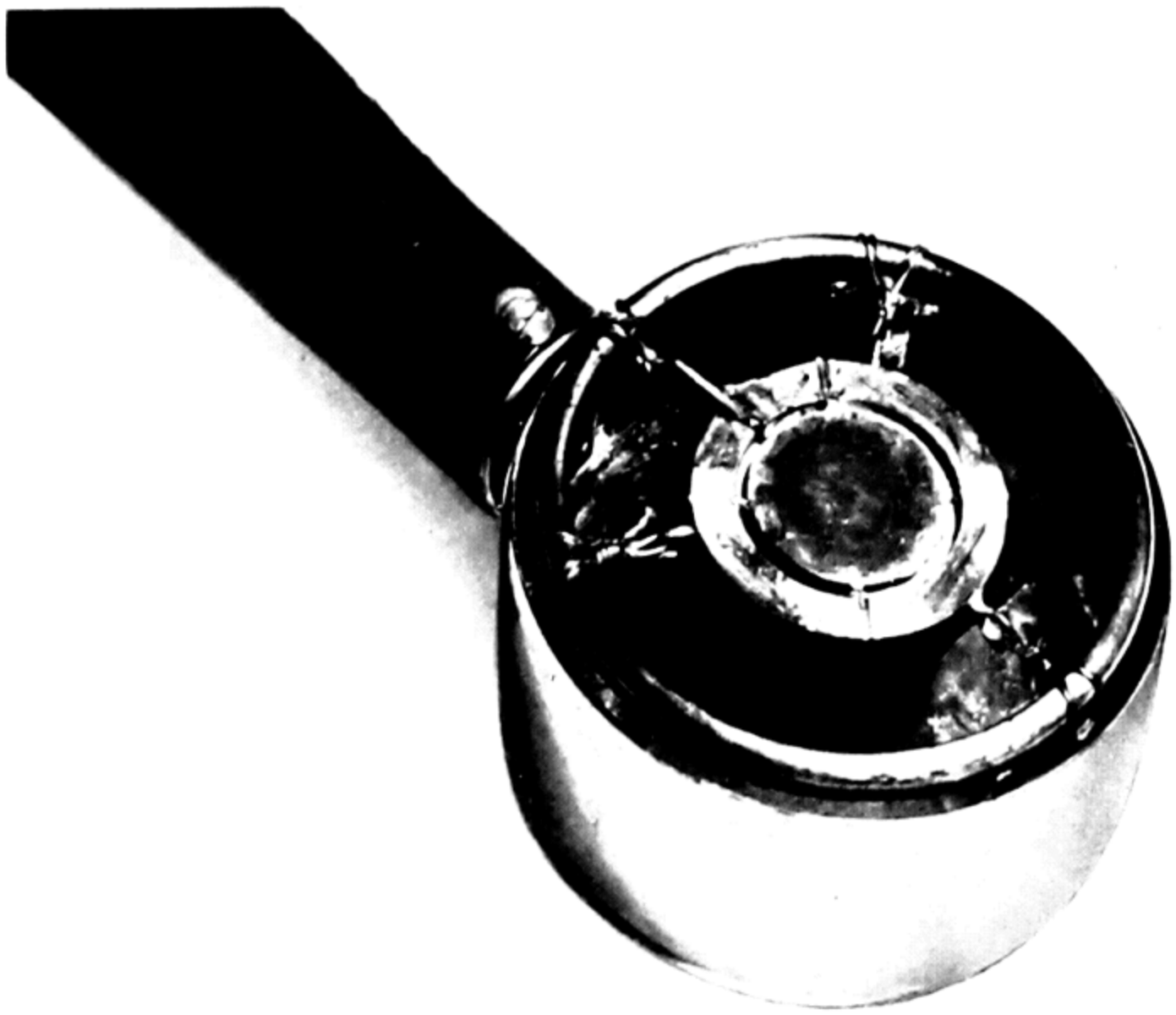
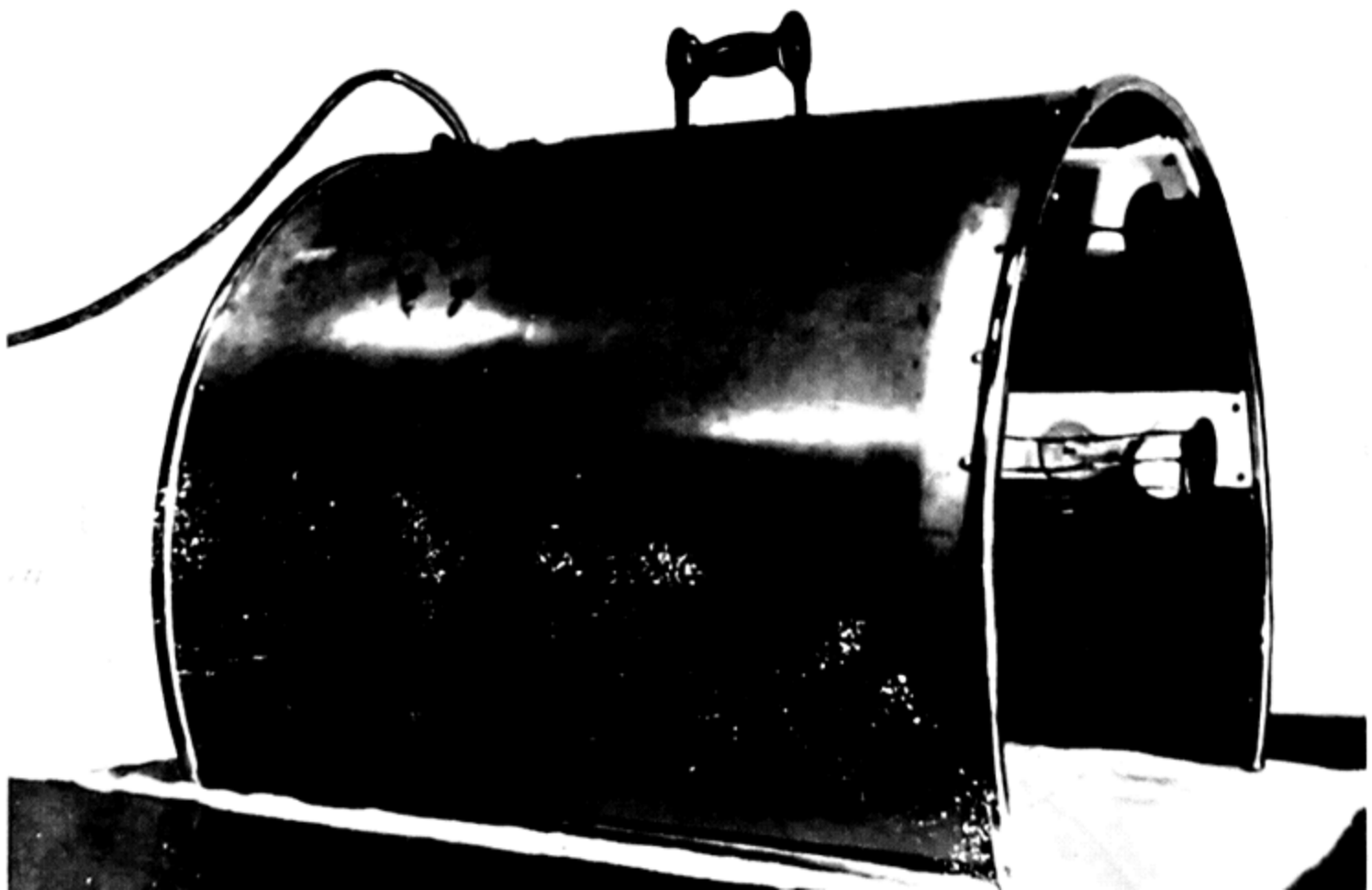


FIGURE 3 – *Radiation fluxmeter. The upper receiver disk, supported on a copper block, is visible. The lower disk faces the water jacket forming the base of the instrument. Water tubes and electrical leads pass through the handle.*

FIGURE 4 – *Radiant heat cradle. (For experimental purposes the inside surface of the metal horseshoe has been blackened.)*



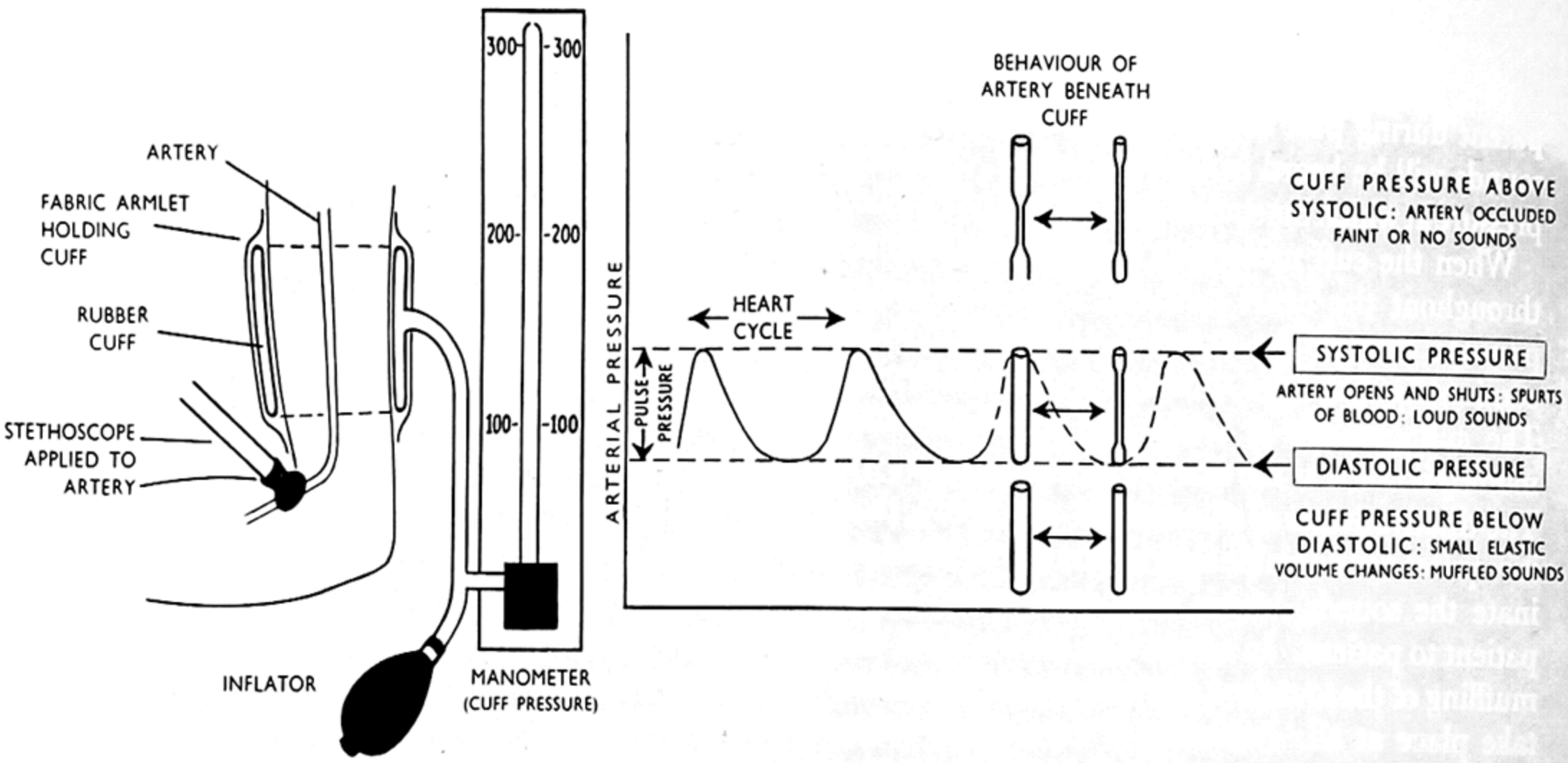


FIGURE 5 – *Schematic representation of blood-pressure determination by use of a stethoscope.*

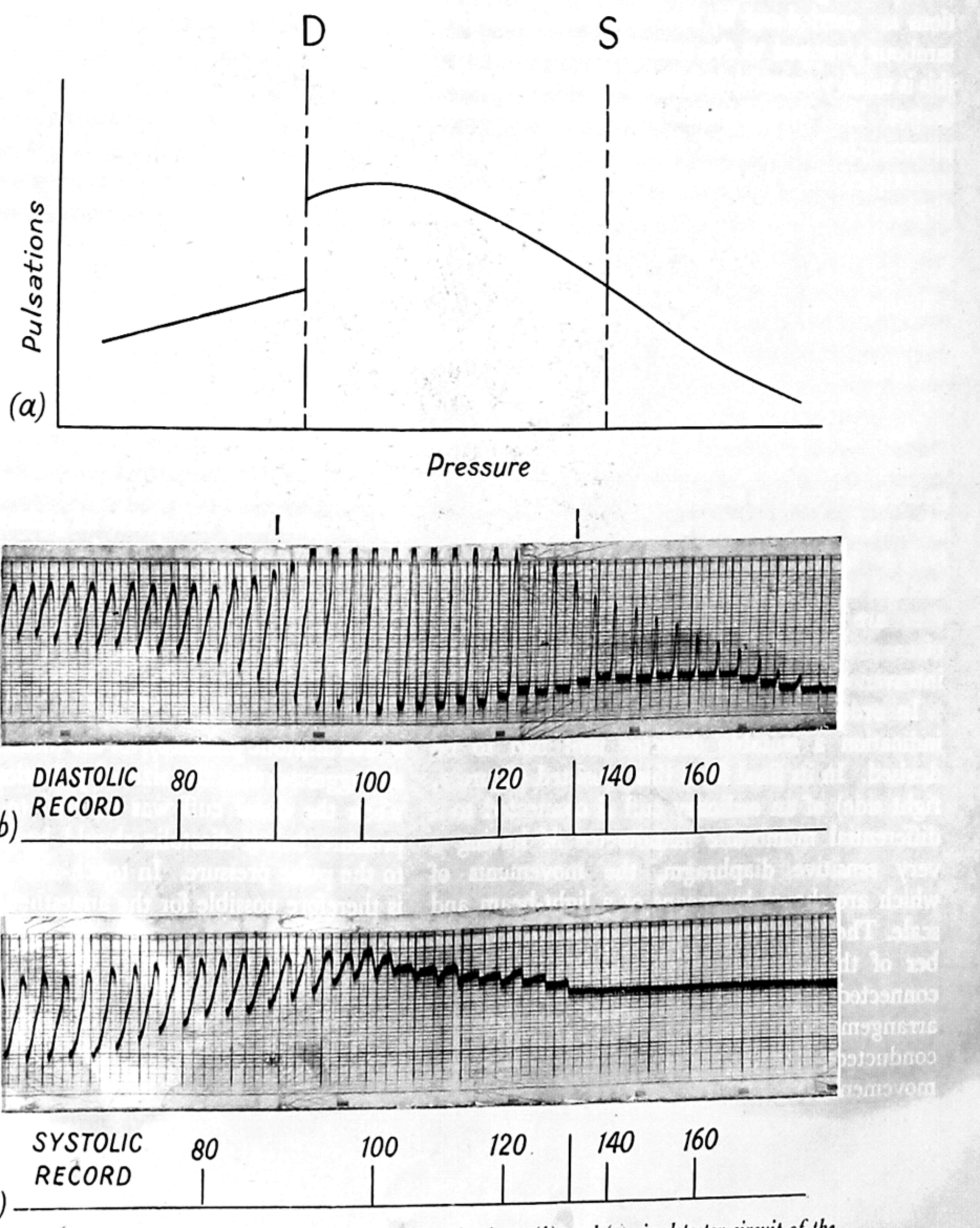


FIGURE 6 – *Theoretical curve (a) and recorded pulsations (b) and (c), in detector circuit of the blood-pressure indicator.* (*Reproduced from the* British Journal of Anaesthesia.)

between systolic and diastolic, the artery will be patent during part of each heart cycle, and loud sounds will be heard in the stethoscope. The cuff pressure at which the sounds start is taken as systolic.

When the cuff pressure is below diastolic, then throughout the heart cycle the internal arterial pressure exceeds the external, the blood-flow is continuous, and faint, muffled sounds are heard. The cuff pressure at which the sounds become muffled is taken as the diastolic pressure (figure 5). The disadvantages of this method are, firstly, that it requires considerable skill accurately to discriminate the sounds, which vary considerably from patient to patient. In a few cases, for example, the muffling of the sounds at diastolic pressure does not take place at all. Secondly, if the work is being carried out under war conditions there may be sufficient noise to drown the sounds altogether. In the operating theatre blood-pressure determinations are carried out by the anaesthetist, using a tambour strapped to the arm of the patient, and this is usually completely inaccessible under sterile drapes. The manipulations of the surgeon may prevent the anaesthetist from securing an uninterrupted hearing of the sounds, or may even displace the tambour, which can never be held in place with the same security as a cuff surrounding the limb, and the anaesthetist may then be left with no means at all of making blood-pressure determinations. In addition, the auditory method is discontinuous, and each determination requires, for the moment, the full attention of the anaesthetist. At the same time, the touch-and-go periods when the anaesthetist has most need of a guide to his patient's condition are precisely those when he is most occupied with restorative measures such as blood-transfusion. Finally, the auditory method can be used only on the arms, and, even if these are not involved in the operation, they are often needed for blood-transfusion, continuous intravenous anaesthetics, and so on.

In order to replace the auditory by a visual indication a suitable detector unit had to be devised. In its final form this consisted (figure 1, right side) of an ordinary cuff *B* connected to a differential membrane manometer *M* having a very sensitive diaphragm, the movements of which are shown by means of a light-beam and scale. The cuff is connected directly to one chamber of the manometer; the two chambers are connected by a capillary *C*. The effect of this arrangement is that rapid pressure-changes are conducted into the first chamber and produce movements of the membrane but are baffled by the capillary; slow pressure changes such as those due to changes in the fluid content of the limb are transmitted, and the mean pressure in the two chambers remains the same. This arrangement allows the use of a membrane giving a full-scale deflection for a pressure difference of a few millimetres of water, such as is produced in the cuff by the arterial volume changes. The system has the advantage that it is entirely pneumatic, and thus the instrument is independent of electric mains.

The nature of the response of this detector unit to arterial pulsations at different cuff pressures is as follows. If the cuff pressure is above systolic, small pulsations are seen; these are due to the impact of the pulse wave on the upper end of the occluded section of artery. Below systolic pressure the artery is patent during a part of each heart cycle, and large pulsations are seen, corresponding to the large volume change from complete occlusion to complete patency. Below diastolic pressure the pulsations are small, and correspond to the small volume changes due to the elastic response of the artery to the pressure changes within it. A closer analysis shows that the transition at diastolic pressure is sharp and forms a good criterion for the determination of diastolic pressure: at systolic pressure there is no sharp change which might be used as a criterion (figure 6).

For the determination of systolic pressure a second cuff *A* is therefore employed, placed proximal to the first. The first cuff and its membrane manometer are employed as a detector unit, and this circuit is inflated to a moderate pressure below diastolic. If now the second, proximal, cuff be inflated above systolic pressure the detector unit will show no pulsations: these will start suddenly when the pressure in the proximal cuff is allowed to fall through systolic pressure (figure 6, systolic record).

A third use of the instrument, which appears to be new, is the possibility of using the distal cuff alone for the indication of pulse pressure (systolic minus diastolic pressure), for the theoretical analysis suggested that the size of pulsations observed when the distal cuff was inflated to a constant pressure below diastolic should be proportional to the pulse pressure. In touch-and-go periods it is therefore possible for the anaesthetist to set the machine to record pulse pressures and to follow them visually while he applies his restorative measures.

The apparatus in its final form is shown in figure 2. The design involved a number of mechanical problems, such as the provision of a

type of totally enclosed, leak-proof tap, and automatic safety devices for the protection of the membrane. The machine has proved robust and has shown itself capable of a number of uses not originally envisaged. For example, it can be used for blood-pressure measurement in the leg, which is not possible by the auditory method. It is applicable to the detection of circulatory abnormalities and to the investigation of rapid physiological changes in the circulation under various experimental conditions. Other developments included a model adapted for photographic recording, and, for the Industrial Health Research Board, a model for recording blood-pressure in the temporal artery while all the limbs were in use [2], [3], [4].

The second problem, drawn from physiotherapy—a particularly fruitful field for physical investigation— concerns the application of infra-red radiation for medical purposes. It is a curious fact that, in sharp contrast to X-rays and gamma rays, the field of medical application of infra-red rays has not been very extensively investigated. Signal exceptions are provided by the researches of such workers as Mayneord and his collaborators [5], and the Medical Research Council has recently established a Committee on Non-ionizing Radiation, which should quickly remedy remaining deficiencies. The reason for this state of affairs is probably to be sought in the differences in physiological action between short-wave and long-wave radiations. In the case of the short waves the most obvious effects are due to specific quantum changes produced in the tissues: these are proportional to the intensity of radiation and often take some time to become fully apparent, so that careful control of dosage is essential. Infra-red radiation, on the other hand, is all in wavelengths so great that the quanta are insufficiently energetic to produce specific reactions, and the only effect appears to be a heating of the tissues, which is noticed almost at once by the patient and can be controlled by the physician. On the other hand, there is a vast difference in scale of the energy used in treatment. In a single treatment, infra-red radiation of a total energy of as much as 20,000 calories may be administered, and doses of this magnitude require careful control, since they approach those capable of causing severe burns, and even of disturbing the general heat-elimination processes of the body.

The specific problem which introduced us to this field arose out of burns caused by a piece of medical apparatus known as a radiant heat or anti-shock cradle (figure 4), which consists simply of a horseshoe-shaped metal sheet fitted on its inner surface with a number of electric light bulbs. This device is placed over the patient and switched on, the object being to keep him warm and to delay the onset of shock. The actual conditions of treatment vary a good deal. Usually the cradle is draped with blankets; sometimes the patient is also wrapped in blankets; sometimes he is treated naked.

The first instruments used in the investigations consisted of various forms of disk receiver forming one junction of a thermocouple, and it soon became clear that a serious time-effect was involved [6]. Evidently the original intention of the metal horseshoe had been to serve as a reflector of radiation, but its real function turned out to be quite different. It actually absorbed a considerable proportion of the radiation, and after an hour or so acquired a fairly high temperature and began to act as a secondary radiator, the area of which was so large that it eventually contributed twice as much as the lamps themselves to the radiation received by the patient. The danger was, therefore, that even if some measuring device were used at the beginning of treatment to determine the dose received by the patient, this precaution would be invalidated by the steady increase in the radiation received. A second point is that this secondary radiation is all in wavelengths so great that it would be absorbed by glass, so that if the treatment were conducted by following the readings of an ordinary glass-enclosed thermocouple, the increase in radiation would not be detected.

It therefore became necessary to devise an instrument for the measurement of radiation flux in all wavelengths, and to recommend that the basis of treatment should always be direct measurement with such an instrument of the actual flux received on the patient's skin throughout the treatment [7]. This recommendation is in contrast to that for X-rays, where the physician relies on calculation of the dosage [8]. It is indeed possible to calculate the infra-red dosage received in any given set of circumstances, but such calculations are too involved to be a feasible method for the ordinary physician.

The instrument devised [9], [10] consists of a pair of disks, carrying thermojunctions on their reverse faces, mounted on opposite sides of a small copper block (figure 3). One disk receives the radiation flux to be measured, while the other is opposed to a water jacket with a blackened surface,

through which water at room temperature is flowing. The construction was aimed at securing a direct-reading instrument responsive to the whole range of infra-red radiation likely to be encountered, accurate to within about 5 per cent., and independent, as far as possible, of the air temperature in which it had to operate. The assessment of the physical factors involved, which were concerned with the transfer of energy by radiation and conduction under conditions removed from thermodynamic equilibrium, proved surprisingly tricky. The final instrument, which shows a linear response to radiation flux, seems to approximate to the best compromise between a number of conflicting physical requirements, and fulfils the conditions imposed reasonably satisfactorily. It also satisfies the medical requirements of robustness, ease of reading, and cheapness of construction. It should therefore now become possible to develop a satisfactory quantitative control of infra-red treatment leading to a better understanding of the effects of this type of therapy. The most important deficiency at present is that so far it has not proved possible to obtain independent measures of the radiation in various spectral ranges, but this is not a serious defect, since, as far as is now known, there is little difference in therapeutic effect between different infra-red wavelengths except for some difference in depth of tissue penetration.

It may be of interest to recall some of the other types of problem dealt with in this general programme. They ranged from the development of methods for the measurement of pressures in small anatomical cavities [11], such as the middle ear; the manufacture and use of devices for measuring subcutaneous [12] and skin-temperature [7], [13], and the construction of a device for the accurate measurement of the volume of a limb; to theoretical analyses of the processes involved in the transmission of light through tissues [14].

It should be pointed out that this account is of a partial nature and is concerned mainly with the work with which the writer has been concerned, but it would be unfair to omit to note some of the more important work which has been carried out by other workers in the field. An excellent summary of work done in Great Britain is provided by the *British Medical Bulletin*, **3**, 6, 1945, containing a general introduction by Professor Mayneord, whose work on infra-red radiation has already been mentioned; an article on biophysical factors in drug action by Dr H. Hurst; a survey of the application of electronics to medicine by Dr G. E. Donovan; and a discussion of the physical factors involved in the causation of brain injuries by Dr A. H. S. Holbourn. The wide field of the applications of electronics to medicine, the recent development of the use of artificially radioactive substances in physiological investigations, and the use of increasingly high-voltage X-rays and of neutrons in medical treatment [15], are among the most striking applications of physics to medicine. They have already attracted a considerable number of workers, particularly in the United States, but it has been our own experience, which is borne out, for example, by Dr Holbourn's fruitful application of the classical notions of elasticity and hydrodynamics to the study of brain injuries [16], [17], [18], that there remains a very large field in which less spectacular physics may aid medicine.

REFERENCES

[1] EVANS, DAVID S., and MENDELSSOHN, K. 'Physics in Wartime Medicine,' *Chemical Products*, January–February 1942.

[2] *Idem.* 'The Physics of Blood Pressure Measurement,' *Proc. Phys. Soc.*, **54**, 211, 1942.

[3] *Idem.* 'A New Instrument for Visual Determination of Blood Pressure,' *Proc. Roy. Soc. Med.*, I, **36**, 465, 1943; MALLINSON, F. BARNETT. *Ibid.*, II, **36**, 465, 1943.

[4] EVANS, D. S., MENDELSSOHN, K., and MALLINSON, F. B. 'A New Sphygmoscope,' *Brit. Journ. Anaes.*, **39**, No. 3, 1945.

[5] MAYNEORD, W. V., and TULLEY, T. J. *Proc. Roy. Soc. Med.*, **36**, 411, 1943.

[6] BROWN, G. MALCOLM, EVANS, DAVID S., and MENDELSSOHN, K. 'The Action of Radiant Heat Cradles,' *Brit. Med. Journ.*, **I**, 66, 1943.

[7] EVANS, D. S., and MENDELSSOHN, K. 'The Estimation of Heat Radiation in Chemical Practice,' *Brit. Med. Journ.*, **II**, 811, 1944.

[8] MAYNEORD, W. V. *Proc. Phys. Soc.*, **54**, 405, 1942.

[9] EVANS, D. S., and MENDELSSOHN, K. 'The Clinical Application of Heat,' *Brit. Med. Bull.*, **3**, 143, 1945.

[10] *Idem.* 'The Physical Basis of Radiant Heat Therapy,' *Proc. Roy. Soc. Med.*, **38**, 578, 1945.

[11] *Idem.* 'Pressure Measurement in Small Anatomical Cavities,' *Lancet*, 8th April, 465, 1944.

[12] MENDELSSOHN, K., and ROSSITER, R. J. *Quart. Journ. Exp. Physiol.*, **32**, 301, 1944.

[13] BROWN, G. M., and MENDELSSOHN, K. *Brit. Med. Journ.*, **I**, 391, 1944.

[14] EVANS, DAVID S. 'Problems of the Transmission of Light through Tissues and some other Media,' *Phil. Mag.*, Ser. 7, **35**, 300, 1944.

[15] SPEAR, F. G. 'Medical Uses of the Cyclotron,' *Journ. Sci. Inst.*, **22**, 21, 1945.

[16] HOLBOURN, A. H. S. *Lancet*, **2**, 438, 1943.

[17] *Idem. Ibid.*, **I**, 483, 1944.

[18] *Idem. Journ. Neurosurg.*, **I**, 190, 1944.

Aerial photography

C. H. WADDINGTON

Cartography is a science essential in both war and peace, though historically the main impulse to the making of maps has been military: the Ordnance Survey was originally a branch of the Royal Artillery, and Napoleon's campaigns led to the first detailed maps of France. The war of 1939–45 stimulated the effective development of cartography by means of aerial photographs. Professor Waddington discusses the possibilities and limitations of the method, and shows the importance of aerial photography for peaceful purposes.

It is well known that during the war aerial photography was one of the most important means of finding out what was going on in enemy countries. In the early days, when Britain was expecting an invasion, it was vital to know if, and where, the Germans were collecting barges and landing craft: it was a task for the Royal Air Force, with its cameras, to keep a continual watch on the Continental ports. Later it had to provide the information by which we could judge the success of our bombing offensive, and the effectiveness of various types of attack. Through the newspapers we became familiar with aerial photographs of acres of devastation in German cities. But these were only the most spectacular, and the most fully publicized, of the achievements of aerial photography. In a more general sense we can say that this technique has become the modern equivalent of cartographic surveying. Generals have always demanded the fullest possible information about the country in which they are to fight, and this demand has been one of the crucial arguments which have persuaded countries to undertake the laborious work of preparing accurate maps. The connection between map-making and military affairs is reflected in the name of the official agency for mapping Great Britain—the Ordnance Survey—which was originally a branch of the Artillery. Similarly, the official maps of France are those originally produced by Napoleon for military purposes.

A century or more ago the military demand for information about potential battlefields was generally met by a survey, conducted on the ground, which recorded only the physical shape of the solid earth and the main features such as roads and towns. Nowadays aerial photography provides not only an accurate map of the same features but also a very detailed account of the nature of the land surface. This may often be of fundamental military importance: a commander will want to know not merely that there is an open area between two roads, represented by a blank space on the map, but much else besides; is it hard ground suitable for tanks, or swampy, or covered in bushes? All this can easily be read from the aerial photographs, and expert examination can extract an extraordinary wealth of information from them. Much of this is, of course, of even more importance for peacetime pursuits than for warlike ones. Normal cartographic maps, prepared originally for soldiers, are recognized as essential tools for all kinds of civil enterprises, not only for legal battles about boundaries, but for every major undertaking of engineering or construction. Aerial photographs, because of the more complete information they may contain, will become the new form of map essential for undertakings of agricultural development, forestry, control of erosion, and so on. The military organization built up for interpreting aerial photographs during the late war is likely to be gradually absorbed, in some form or other, into the service of civilian affairs, just as the Ordnance Survey was in an earlier period.

This does not necessarily mean that surveying on the ground has gone out of date. It will probably remain for some time a better method of obtaining extreme accuracy than surveying from the air. If we are concerned only to produce a physiographic map of the normal kind, the advantages of the air are not in greater accuracy but in rapidity. It is, for instance, obviously very easy to use aerial photography to make frequent revisions of an already existing map, so as to keep it up to date. There are even greater advantages in undeveloped countries where travel is difficult. Aerial photography can be used to fill up the spaces in a grid of points whose position has been fixed by triangulation on the ground, but it will probably soon be possible to dispense with all ground control over very wide areas. Experiments

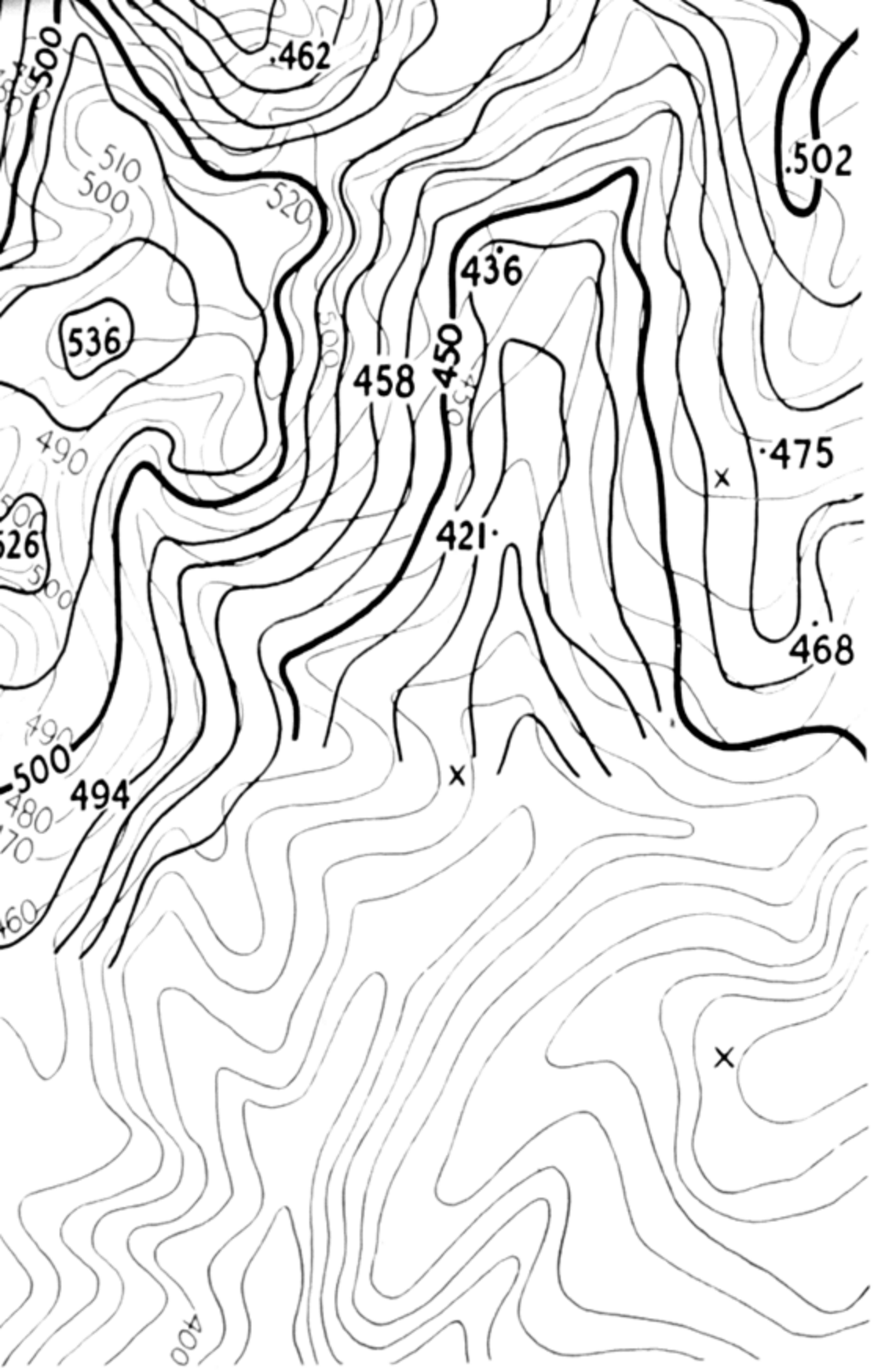


FIGURE 1 – *Comparison of contours based on the use of radar fixes (heavy lines) to locate the photographing aircraft in space, with the contours recorded by accurate ground survey. (Contours at 100 ft. intervals.) The material was worked out from one of the first experimental flights, the nearest ground station of the radar system being 85 miles away.*

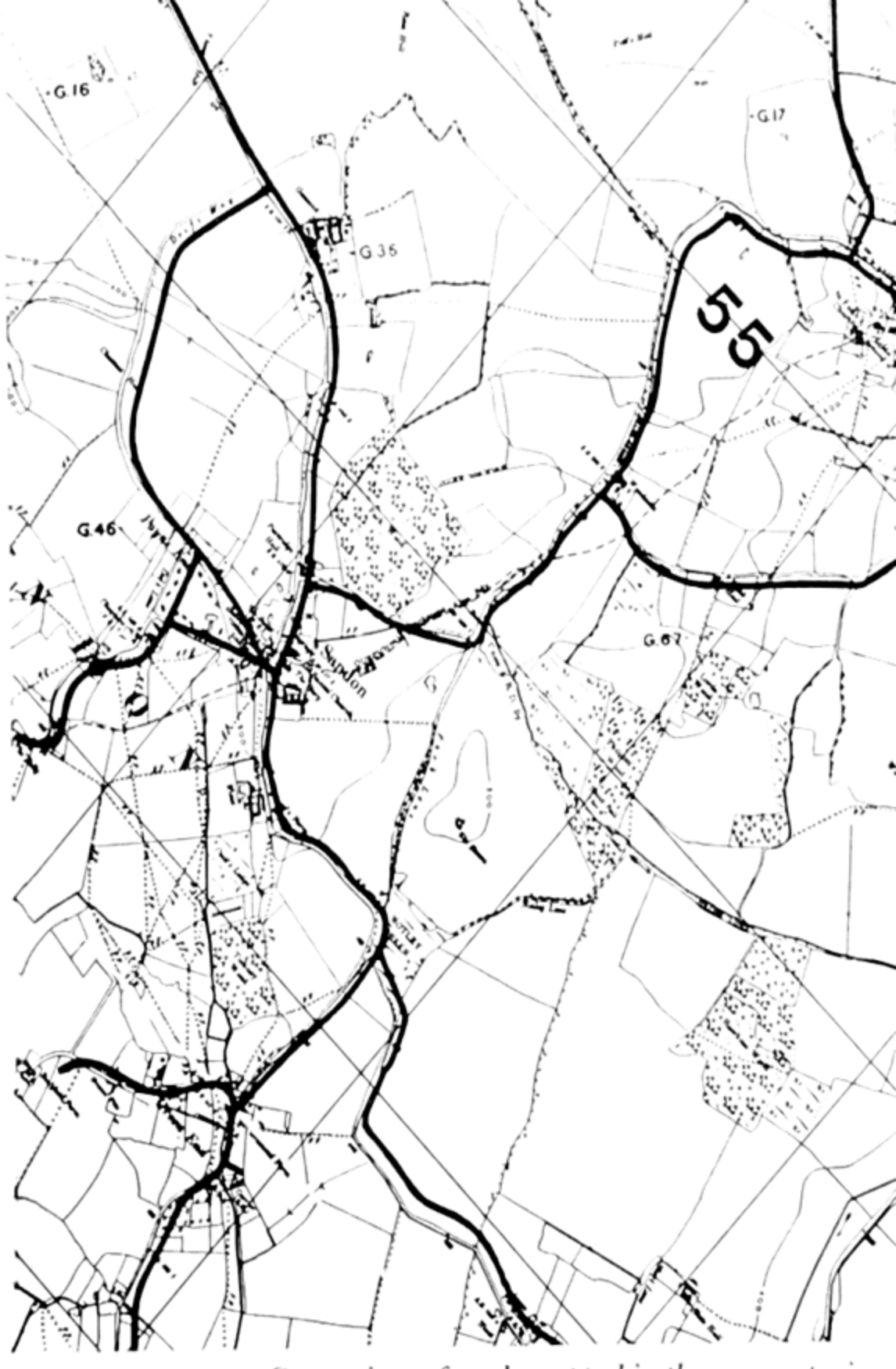


FIGURE 2 – *Comparison of roads mapped in the same experimental radar-controlled flight with those recorded by ground survey. (The roads mapped by radar are printed in black.)*

FIGURE 3 (*below*) – *Venice, showing the Piazza S. Marco.*



FIGURE 4*a* – *Boulogne harbour at low tide, with the dredged channels showing up clearly.*

FIGURE 4*b* – *Boulogne harbour during the maximum spring tides, showing how a whirlpool is formed in the mouth of the harbour by silt-laden water.*

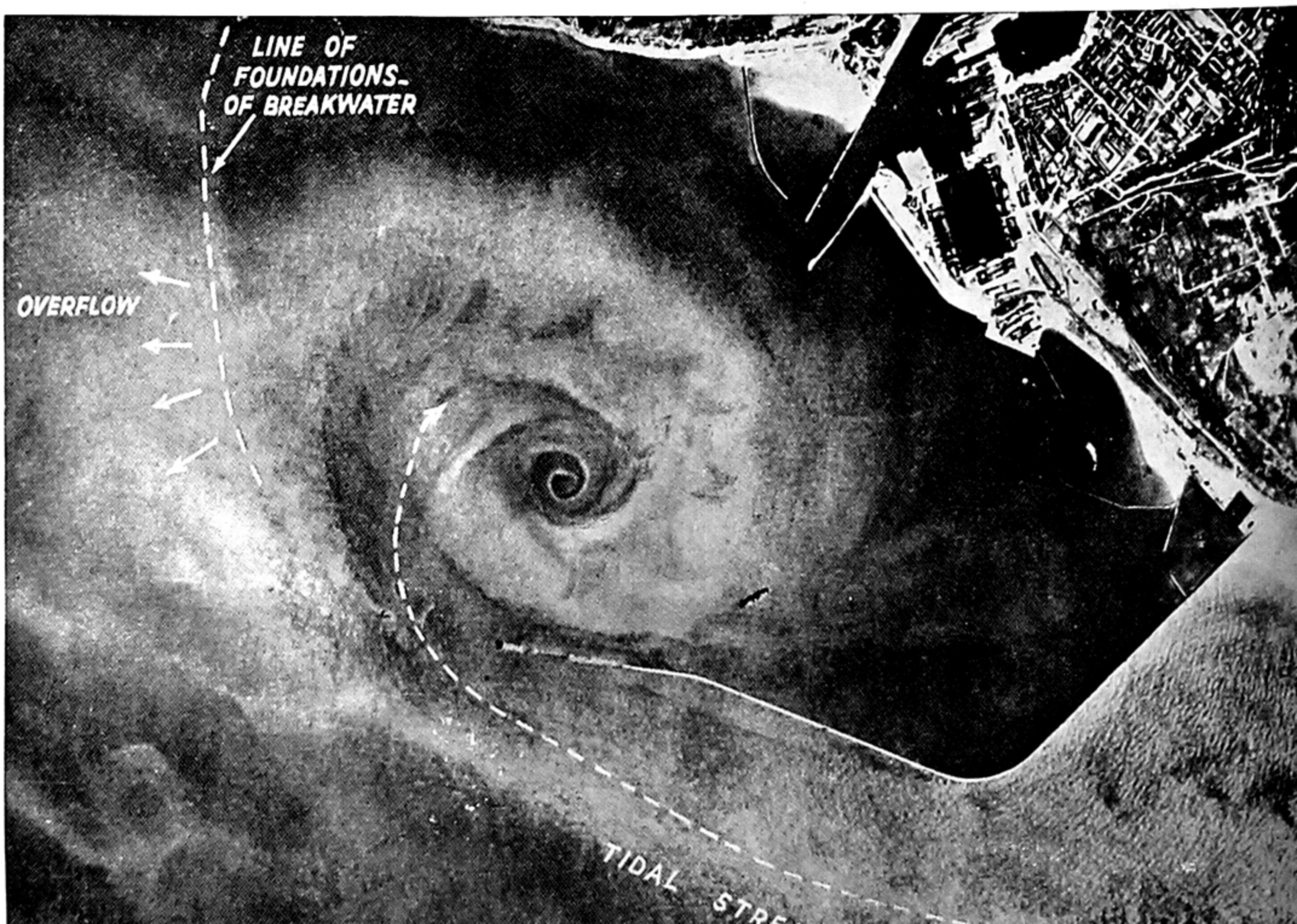






FIGURE 5 – *Three photographs, taken through (a) green, (b) red, and (c) infra-red filters, of a sandy cove in Cornwall. Notice the steeper gradation of tone in the sea on the red photograph in comparison with the green one. Notice also the position of the water-line, which is sharply revealed by the infra-red.*

FIGURE 6 (*below, right*) – *An oblique photograph, showing the eighteenth-century Dutch gabled houses in the Grande Place at Arras.*



FIGURE 7 – *A tongue of terraced paddy fields extending up a small valley.*



FIGURE 8 – *A village with scrub on one side, and, on the other, fields with ground-nuts and similar crops.*

FIGURE 9 – *Most of the larger fields shown here contain bush crops such as tobacco, but there are also some small rice fields in the low-lying parts.*



FIGURE 10 – *A coco-nut plantation, with deciduous forest behind it. The beach is a coral reef.*



FIGURE 11 – *In this difficult country, two types of jungle can be easily distinguished.*

FIGURE 12 – *The hills at the top of the photograph are covered with relatively untouched jungle, but over most of the area the hillsides have been felled and burnt, the land used for a few crops, and then allowed to revert again to forest.*

FIGURE 13 – *A cultivated plain, beginning to suffer badly from erosion along the valleys.*

FIGURE 14 – *Houses set amid coco-nut groves, photographed with a moving-film camera* (*page 84*).



FIGURE 15 – *Den Helder, a Dutch town which is nearly enclosed within its ancient fortifications.*

are now proceeding on the use for survey purposes of some of the radar devices which were developed to aid the navigation of a bomber to its target at night. By means of these instruments one can determine the position of the aircraft, relative to the two or more ground stations transmitting the signals, at the instant of photography. Very accurate maps can then be made up to distances—at present—of a few hundred miles. An example, from one of the first experimental flights, is illustrated in figures 1 and 2. This technique is very rapidly advancing, and it is likely that it will soon be able to play an important role in surveying many comparatively undeveloped regions of the world.

One rather specialized branch of surveying work in which the cheapness and speed of air photography show to unexpected advantage is the investigation of the under-water topography near the shore. By choosing favourable conditions of wind, sun altitude, and other factors, it is possible to take aerial photographs which register details of the bed of the sea down to twenty or thirty feet, which is deep enough for most practical purposes of coastal navigation. Figure 4 shows how one can get an overall picture both of the success of harbour dredging and of the currents which bring in the silt. These photographs were taken in routine reconnaissance. Much more exact information can be obtained by special techniques. Perhaps the most generally useful of the latter is simultaneous photography through red and green filters. Through a green filter the bottom can be seen to a greater depth than through a red one; in a green-filter photograph the graduation in tone from the shore to the black of the deep sea will therefore be more gradual than in a red photograph (figure 5). By expert comparison of the two photographs depths can be determined with considerable accuracy, the maximum range depending on the nature of the bottom, the muddiness of the water, and other factors. This type of interpretation can be reliably done only by experts, but their results compare very favourably with those obtained directly by the laborious process of taking soundings (figure 16).

It is when the aerial photograph is considered as a supplement to a map, giving information which is normally not plotted by cartographers, that its greatest advantages appear. For town planning, for instance, a set of air photographs will not only give an accurate picture of all the recent additions to the town and make it possible to work out the heights of buildings as well as their plan position, but will show the character of the town in a vivid and realistic way which is quite impossible on a map. The town planner can get his photographs at the scale which is most appropriate for his particular interests (figures 3, 6, and 15). He may want to study a whole region, and the relation between town, agricultural land, forests, parks, hills, and so on; or he may be interested in more detailed matters. In any case the air photograph will present the material in a way which, unlike the normal map, does not omit the aesthetic qualities on which good town planning so largely depends.

Another most important use of aerial photography in peacetime will be for the preparation of land-utilization maps. One can, of course, very easily distinguish the main categories of land—arable, grassland, woods, parks, and so on; and land-utilization maps can be made which are not out of date before the survey has been completed, an achievement which is scarcely possible when such maps are made from ground studies unless a prohibitively large staff is employed. From aerial photographs, moreover, one could go into considerably greater detail than is worth attempting in ground maps which can be revised only at long intervals. Many of the most important crops can be distinguished in photographs on quite a small scale. More research is still needed on this type of interpretation; many of the appearances presented by crops at different stages of their growth are somewhat unexpected and deceptive to the layman, but it is clear that we can already get much more up-to-date information about the purposes for which land is used than has been available before.

This may be of particular importance in regions which are comparatively undeveloped, where agricultural statistics are usually even more incomplete than in the longer-settled countries. Figures 7–11 show some typical examples of various agricultural crops growing in Burma: clearly from such photographs one could make fairly exact estimates of the acreage used for different purposes. Moreover, the administrator can keep a continual check on the fleeting cultivations which some semi-nomadic peoples set up in the jungles (figure 12), and can discover when the burning of the cover of trees is going too far, or erosion is becoming dangerous (figure 13). A valuable indication of forest resources can also be obtained: the main ecological types of forest can be mapped, and, if necessary, the supplies of

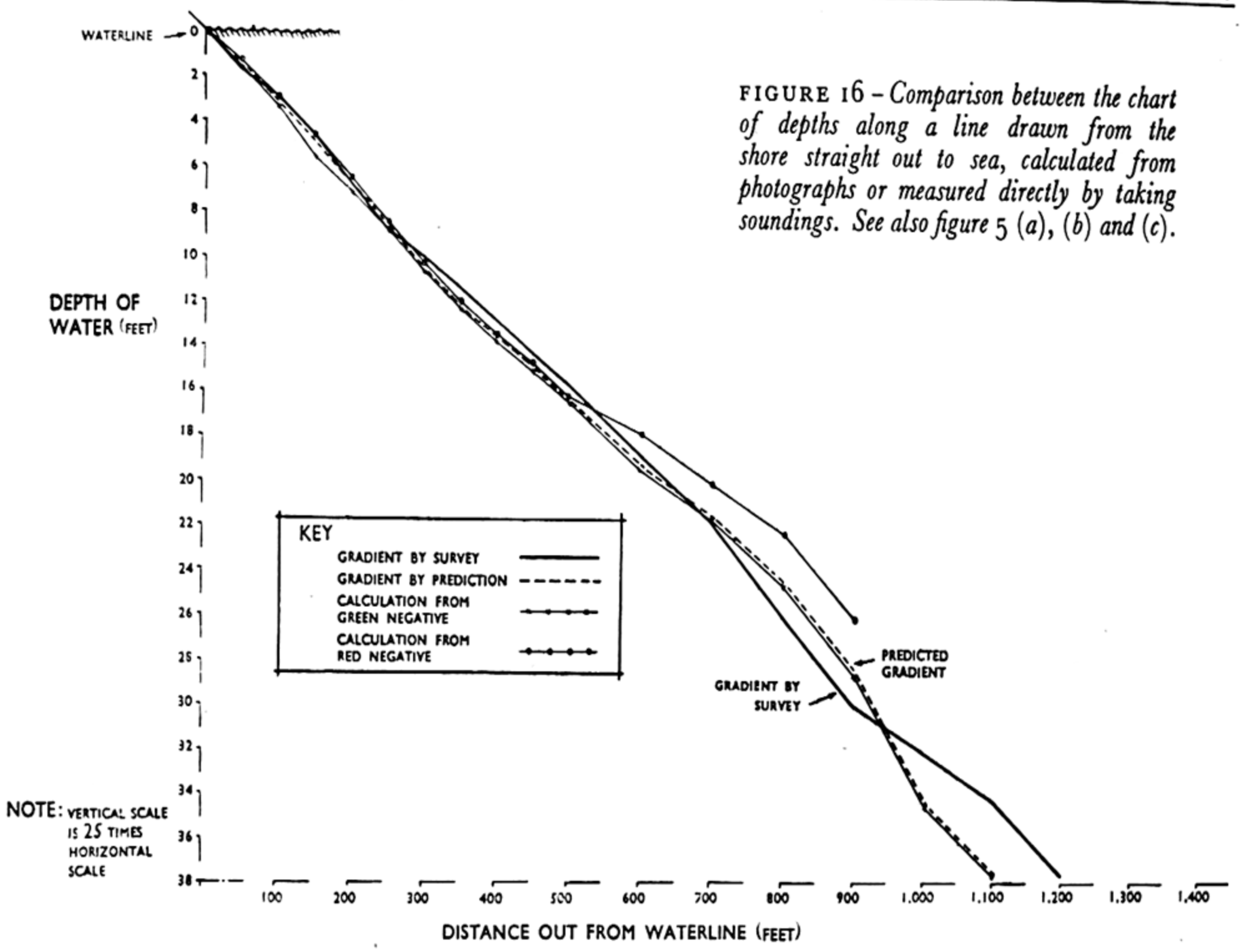


FIGURE 16 – *Comparison between the chart of depths along a line drawn from the shore straight out to sea, calculated from photographs or measured directly by taking soundings. See also figure* 5 (*a*), (*b*) *and* (*c*).

particular trees such as teak or wild rubber estimated.

There is another wartime technical development which has a certain contribution to make to vegetation surveys and similar projects. This is the moving-film camera, in which the film can be moved during the exposure so as to compensate for the movement of the image caused by the speed at which the aircraft is travelling. This compensation is of importance only when high-speed aircraft are travelling rather low down. With this system it is possible to take sharply focused vertical photos at such large scales that they eliminate the need for any checking on the ground of the accuracy with which the usual small-scale photos have been interpreted (figure 14). This has great advantages in inaccessible country. If, for instance, one wishes to be certain of the different species of trees in a region like that shown in figure 11, it would be tedious to have to send an expedition to verify the photo-interpretation; but the job could be done quite quickly with a low-level, vertical photograph of this kind.

There has been space to mention only a few of the uses of aerial photography for peaceful purposes. Those which have been chosen for illustration are those which can be most generally applied to almost any region of the earth. Many other applications have been made more locally. For instance, in some countries aerial photos clearly show the boundaries of different soil areas. In some parts of the world, particularly uncultivated countries, a great deal of geological information can be deduced from them, and rough geological surveys can be made with a minimum of ground work. There have also been many quite local problems where air survey has been extremely valuable—for siting reservoirs, power cables, roads, and so on. Much use has also been made of the method in archaeological work for discovering the position and extent of ancient fortifications, circles, burial mounds, and other artifacts. It would take too long to try to enumerate all these possibilities, and in any case the list would certainly be incomplete. Enough has been said to show that in aerial photography we have another technique which can supplement ground mapping with new applications of as wide, though somewhat different, a scope.

The spectroscopy of flames

R. F. BARROW

Flame spectra are very complex, and it is only since the development of quantum theory that substantial progress towards their elucidation has become possible. Difficulties may arise owing to the necessity for distinguishing between chemiluminescent and thermal phenomena. Dr Barrow here reviews recent work, and makes the interesting point that chemiluminescence may in the future have an important part to play in lighting systems.

Recognition of spectroscopy as a valuable tool for investigating the nature of flames dates from the work of Bunsen and Kirchhoff, published in 1859. Their fundamental observation that elements are characterized by spectral lines of definite wave-length stimulated the empirical study of spectra, of which the most striking results were the discovery of new elements and Crookes's identification of Lockyer's line in the solar spectrum with that derived from terrestrial helium. Such line spectra were attributed to emission of light from atoms, and band spectra to emission from particles of greater complexity, but in the latter case experimental evidence was by itself insufficient to identify the emitters unambiguously. The interpretation of band spectra had to await quantum theory, the application of which to the analysis of the spectra of simple molecules, particularly those consisting of only two atoms, was finally worked out in the period 1925–35.

The study of flame spectra followed this general development, so that the earlier work was directed mainly towards identification of atomic and molecular species. The results of this work were somewhat surprising. It was manifest that flames consist of mixtures of reacting gases, sometimes with dispersed solid smokes, often at fairly high temperatures. That they contain unusual chemical species was evinced by their electrical conductivity. That certain atomic spectra, for example those of the alkali and alkaline earth metals, were found to be of frequent occurrence was not unexpected. The vapours of these elements were known to be largely monatomic, and the actual atomic concentrations required for light emission were found to be exceedingly small. What was at first remarkable was the nature of the molecular species identified—unstable radicals, unknown to the chemist under ordinary conditions, such as C_2, CH, and OH. Analysis of the fine structure of their spectra, however, left no doubt of the correctness of their identification, while at about the same time their existence under such conditions became more readily credible as workers in the field of chemical kinetics found it necessary to postulate their participation in photochemical and thermal chain reactions.

Apart from the line and band spectra, which may be characterized, if not always in the latter case immediately identified, by wave-length measurements, many flames emit continuous spectra the elucidation of which necessarily requires more subtle experimental investigation. Such continua may arise either from incandescent solid particles present in the flame or from a variety of atomic and molecular processes, some of which will be considered later.

The first problem in the study of flame spectra must always be the identification of the emitting species. This often presents experimental difficulties which increase with increasing weight and complexity of the emitter. Even in diatomic spectra the only certain methods depend either on rotational analysis, which gives information about the molecular quantum numbers and the interatomic distances, or on comparison with absorption spectra obtained under clearly defined chemical conditions. Both methods are subject to limitations. Rotational analysis requires the use of large spectrographs of high resolving power, but the amount of light available in flames is frequently very small, so that the necessary length of exposure may be almost impracticable. In addition, in presence of the continuous radiation which so frequently accompanies the discrete spectra, it may be difficult to secure adequate contrast of the structure lines on the photographic plate. The method of comparison with absorption spectra is of course confined to those systems which involve the ground electronic state of the radical concerned (which is, however, very often in this state), and to those species which are of not

too great chemical instability. In spite of these difficulties it has been possible to identify with certainty a high proportion of the diatomic radicals whose spectra occur in flames, and indeed, owing to their particular excitation characteristics, the reverse process has sometimes been employed, i.e. flames are sometimes useful sources for the spectroscopic examination of molecules which do not appear to emit light readily under other experimental conditions.

The difficulties of identification are greatly multiplied in the flame spectra of radicals or molecules containing more than two atoms. In place of the definite answers which spectroscopy can give about atomic and diatomic emitters, the identification of the substances responsible for electronic band systems of polyatomic molecules is much less certain. It then generally becomes necessary to take into account more ambiguous evidence, relating for example to the probable concentrations of transitory intermediates. At least three such systems—the carbon monoxide and hydrocarbon flame bands and the ammonia α-band—are of some importance in connection with theories of combustion, and it is unfortunate that in no case is the identity of the emitter immediately demonstrable.

The spectrum of the flame of carbon monoxide burning in air or oxygen consists of a faint system of bands superposed on a strong, continuous background which extends through the visible and near ultra-violet regions of the spectrum, and is strongest in the range 3,500–4,500 A. It has been concluded that the emitter is probably carbon dioxide [1], [2].

The ethylene, or hydrocarbon, flame bands, which lie in the range 2,500–4,500 A, are associated with the flames of burning hydrocarbons: they occur, for instance, in the inner cone of the ordinary Bunsen flame, and were first described in detail by Vaidya [3]. Gaydon has studied this spectrum recently [4], and has shown that its production runs parallel with the formation of peroxides in the flame. Like Vaidya, he assigns the bands provisionally to HCO, but remarks that alternative emitters cannot be entirely ruled out.

The ammonia α-band, a complex 'many-lined' spectrum, appears in the oxy-ammonia flame, and is responsible for its yellow-green colour. It has been ascribed by Rimmer [5] to NH_2.

The study of continuous spectra has been somewhat neglected by spectroscopists, perhaps naturally enough in view of the abundance of discrete spectra to be photographed and analysed, but as a result of this preoccupation there is surprisingly little quantitative information available about continua. And it is quantitative information which is now in question, for the only means of characterizing such spectra precisely is by way of data giving the intensity of the continuum as a function of wave-length, i.e. of energy. Before discussing any individual examples it will be as well to consider briefly some of the possible mechanisms by which light can be produced in flames.

The ultimate aim of quantitative spectroscopy is to relate the intensity to the probability of the particular event leading to light emission at a given wave-length and the number or numbers of particles involved in that act. The general formulation of this problem was given by Einstein. Considering the transition from an excited state 1 to the ground state 0, for the total energy emitted per unit time per unit volume, $\bar{S}_{1,0}$ we have:

$$\bar{S}_{1,0} = N_1.h\nu_{1,0}.A_{1,0}$$

where $\nu_{1,0}$ is the frequency of the light emitted,

N_1 is the number of atoms or molecules per unit volume in state 1, and

$A_{1,0}$ is the 'transition probability,' which is often given simply by the reciprocal of the life-time in the excited state, τ_1.

The processes responsible for light production can be divided broadly into two classes: (*a*) thermal excitation, and (*b*) chemiluminescence, and we will take these in turn.

It appears probable that, in many flames at least, the mechanism of light emission by radicals or solid particles is due merely to collision with charged or uncharged molecules or with atoms possessing high thermal energies. On a simple view, if we assume that temperature equilibrium is established for the different modes of energy intake, we can apply the Boltzmann distribution law to get the number of particles in the upper state N_1, and we find that there should be an exponential dependence of $\bar{S}_\lambda$ (the value of $\bar{S}$ at some wave-length λ) upon absolute temperature T of the form $\bar{S}_\lambda = C.e^{-h\nu/kT}$, where C is a constant. The interest of this expression is that, although it is experimentally very difficult to measure absolute values of the intensity—indeed reliable measurements have been made for only a few atoms and for one or two diatomic molecules such as OH and CN—we can get relative intensity values without too much difficulty, and such data provide the basis of the spectroscopic methods of temperature determination.

For this, the distribution of molecules among either vibrational, or, better, rotational, states may be used. Alternatively, and far more conveniently, the line-reversal method can be employed. The principle of this is as follows. The reversal of spectral lines, e.g. the sodium *D* lines excited by adding small amounts of a sodium compound to the flame, is examined in a visual spectrograph against a background of variable brightness such as may be obtained from a tungsten strip filament lamp. When the lines just merge into the continuous background the flame and the continuous source are at the same black-body temperature, which may be measured on the latter with an optical pyrometer. It should be mentioned that there has been some criticism of this method, directed against its basic assumption that the atomic radiation is purely thermal, but that it does apply in a fair number of cases is shown by data quoted, for example, by Jost [6].

The variation of the intensity of emission with wave-length at a constant temperature is, of course, different for different cases. A continuum arising from incandescent particles would obey Planck's distribution law for black-body radiation—or rather the law as modified for a grey body, taking into account the departure from unity of the emissivity of the particles. Unfortunately, emissivity data, except for a few technically important substances, are rather meagre. In the case of discrete or continuous light emission arising from a transition between two electronic states, the wave-length distribution of intensity will depend upon the relative disposition of the potential energy surfaces in upper and lower states (Franck-Condon principle), on the statistical weights of these and of the sub-states, and on the Boltzmann distribution function for the upper state. Since the amount of energy available for thermal excitation in ordinary flames is comparatively small, the discrete electronic systems observed almost invariably involve the ground state as the lower state of the transition. As has already been remarked, it is not yet possible to give any coherent picture of the continuous spectra of flames. One important type results from the recombination of an electron with a positive ion to form a neutral atom. A continuum whose origin seems to be still somewhat in doubt, but which is remarkable for its intensity, is that which appears more or less symmetrically disposed with respect to the resonance lines of sodium and potassium (and presumably the other alkali metals) when the metal is burned in oxygen or is introduced into a hydrogen-air flame or into the hollow cathode of a Schüler tube. Preliminary observations on the sodium-hydrogen-air flame suggest that the intensity is proportional to the concentration of alkali metal, and that it may have a temperature coefficient of the order expected for thermal excitation.

When a mixture of carbon disulphide and nitric oxide is exploded a brilliant flame is produced, which from the quantity of light emitted (apparently largely from the S_2 band spectrum) would correspond to black-body radiation at a temperature of about 5,000° K [7]. Again, under certain conditions, it is possible to get organic substances such as ether, acetaldehyde, and hexane to react with oxygen at rather low temperatures (200–400° C) with simultaneous emission of light. The latter flames have been photographed by Emeléus, and the spectra, which are all identical, have been shown by Pearse to be due to formaldehyde. It is clear that there is no direct relation between the temperatures of such flames and their luminosity, and it must be concluded that the light emission is due to some chemiluminescence process, whereby sulphur in the former case and formaldehyde in the latter are produced in excited electronic states. Let us briefly consider what might be expected of such a process.

The fundamental distinction between chemiluminescence and thermal excitation depends on the predicted numbers of excited species, N_1.† If, for example, a radical C is formed in an upper state by a chemiluminescence reaction

$$A + B \rightarrow C^*,$$

C^* thence falling back to the ground state with emission of radiation,

$$C^* \rightarrow C + h\nu,$$

then provided that deactivation processes of the type

$$C^* + M \rightarrow C + M$$

are unimportant, almost every C^* formed will radiate energy, instead of only the Boltzmann fraction of the stoichiometric concentration of species C, $e^{-h\nu/kT}$, for pure thermal excitation. Furthermore, in a chemiluminescence process, the effect of temperature on intensity will be determined by the activation energy of the reaction $A + B \rightarrow C$ (or by that of the rate-determining

†A clear experimental distinction between chemiluminescence and temperature radiation is by way of Kirchhoff's law, which states that at a given temperature the ratio of emissive power to absorptivity is constant and equal to the emissive power of a perfect radiator. This law is based on the assumption of thermal equilibrium and is therefore not obeyed by chemiluminescent systems.

step in the cycle of events which leads to the production of A and B) rather than by the quantity $h\nu$.

The most thoroughly investigated reactions of this type are those between alkali metals and the halogens or halogen-containing compounds at low pressures in the dilute flames of Polanyi. In the case of sodium and chlorine an efficiency of about unity can be obtained for the light emission of the D lines. The most probable mechanism is:

$$\begin{aligned} Na \quad &+ Cl_2 = NaCl \quad + Cl \\ Na_2 \quad &+ Cl \;\; = NaCl^* + Na \\ NaCl^* &+ Na = NaCl \quad + Na + h\nu \end{aligned}$$

where NaCl* refers to a sodium chloride molecule of high vibrational energy content.

The best-known example of a chemiluminescence continuum is again provided by the alkali metals and the halogens, for which recombination spectra due to processes of the type

$Na + Cl = Na.Cl^*$ (homopolar upper state)

$Na.Cl^* = Na^+.Cl^-$ (ionic ground state) $+ h\nu$

have been observed.

So far we have considered the bearing of chemiluminescence alone on electronic energy changes, but it appears also that thermal equilibrium may not always be attained for the other forms of energy intake. Thus the rotational temperatures of C_2 and CH in one and the same discharge through acetylene were found by Lochte-Holtgreven to be 4,700° and 2,000° K respectively. That this is not an unfair example is shown by the vibrational intensity data of Kondratjew and Ziskin [8] for a hydrogen-oxygen flame. They found that the (2, 1) band of the OH system was stronger by a factor of the order of 50 than it should have been had the vibrational energy distribution been thermal. Similar evidence that there is sometimes a delay in reaching equipartition for vibrational energy has been adduced from studies of vibration-rotation bands in the infra-red.

It is of considerable importance to establish whether or not the vibrational or the electronic energy is chemiluminescent or thermal in origin. If chemiluminescence processes obtain, then clearly the scheme postulated for the overall reaction must make provision for the formation of such species in excited levels. It would take us too long to consider any one case in detail—even the mechanism put forward for the burning of hydrogen in oxygen to form water is a formidable affair—but it is worth noting that in this reaction the spectroscopic evidence that the OH emission must be chemiluminescent is of considerable value in assessing the relative importance of some of the different reaction steps suggested.

This question has also a very direct bearing on practical problems of light production. It has already been mentioned that the emission from the carbon disulphide-nitric oxide flame corresponds in efficiency to a black-body radiator at about 5,000° K. It has been calculated to be about 83 lumens/watt. 5,000° K is, of course, an impracticable temperature for a terrestrial flame. If we take 2,000° K as a reasonable figure, we get an efficiency of light production of only 1·7 lumens/watt, so that the chemiluminescent source is, on an energy basis, some fifty times as efficient as an ideal black-body source at 2,000° K. So far, no one has succeeded in developing any such chemiluminescent source on any considerable scale.

Finally it should be noted that spectroscopic measurements in absorption provide us with the possibility of determining the concentrations of radicals. This may be done directly to determine stationary concentrations in flames, but what is probably of greater interest is the possibility of observing changes of concentrations with time in discharges, and thus exploring the kinetics of their production, decay, and transfer of energy. Such studies of radical kinetics are difficult, and the results are not necessarily immediately applicable to the radical reactions occurring in flames, but they should nevertheless form an increasingly valuable supplement to data derived from the more orthodox methods of chemical kinetics.

REFERENCES

[1] Gaydon, A. G. *Spectroscopy and Combustion Theory* (London. Chapman & Hall, 1942).

[2] Kondratjew, V. 'The Carbon Monoxide Flame Spectrum,' *Zeit. f. Physik*, **63**, 322, 1930.

[3] Vaidya, W. M. 'Spectrum of the Flame of Ethylene,' *Proc. Roy. Soc.*, **A147**, 513, 1934.

[4] Gaydon, A. G. 'The Spectra of Chilled Hydrocarbon Flames,' *Proc. Roy. Soc.*, **A179**, 439, 1942.

[5] Rimmer, W. B. 'The Spectrum of Ammonia,' *Proc. Roy. Soc.*, **A103**, 696, 1923.

[6] Jost, W. *Explosions- und Verbrennungsvorgänge in Gasen* (Springer, Berlin, 1939).

[7] van Liempt, J. A. M., and de Vriend, J. A. 'The Explosion of Carbon Disulphide-Nitric Oxide Mixtures,' *Rec. Trav. Chim. Pays-Bas*, **52**, 549, 1933.

[8] Kondratjew, V., and Ziskin, M. 'The Spectrum of the Hydrogen Flame,' *Acta Physicochim. U.R.S.S.*, **7**, 65, 1937.

Molecular sedimentation in the ultracentrifuge

THE SVEDBERG

The sedimentation of particles of molecular dimensions can be experimentally observed if the equivalent of an intense gravitational field is produced by centrifugal force. The necessary conditions can be created in an apparatus known as the ultracentrifuge. The latter has proved particularly useful in the study of the homogeneity of proteins and the determination of their molecular weights. The technique has also been successfully used in the study of other natural and synthetic polymers such as cellulose, rubber, and polyethylenes.

The sedimentation or settling of small particles under the influence of gravity is an everyday phenomenon which plays, and has played, a great part in geophysics. Clay deposits, old and recent, are formed through the fractionating effect of the sedimentation of particles carried by the water of streams and rivers to the lakes and the ocean. With decreasing size of particle the sedimentation becomes slower and slower, until the inevitable thermal convection currents stop it altogether. The greenish colour of many glacier lakes is due to minute particles floating in the water.

If the size of the particles is further diminished, to molecular dimensions, another phenomenon comes into play, namely the diffusion or irregular thermal motion of the individual particles or molecules. The atmosphere surrounding the earth is kept from flying away into planetary space by sedimentation, and is prevented from settling down as a dense layer on the surface of the earth by diffusion. The state resulting from this combination of sedimentation and diffusion is called sedimentation equilibrium. If we want to use the sedimentation of molecules for analytical purposes in the laboratory, the force of gravity has to be increased hundreds of thousands of times. This can be accomplished by means of swift rotation in a specially designed centrifugal apparatus, the so-called ultracentrifuge.

The first measurements of molecular sedimentation were performed at Upsala in an oil-turbine ultracentrifuge constructed for that purpose. Since then other types of ultracentrifuge have been devised, using compressed air or electric current of high frequency as the driving agent. Whatever the driving force, the solution to be studied has to be enclosed in a small cell of sectorial shape with windows for optical measurements. This cell has to be mounted in a rotor spinning at constant temperature in hydrogen at low pressure, or in a perfect vacuum (figure 1).

Particles or molecules in a centrifuge travel towards the periphery along radii, hence the sectorial shape of the cell. Constant temperature has to be maintained in order to avoid disturbing convection currents. In the case of the oil-turbine ultracentrifuge the rotor is provided with two small turbines, one at each end of the shaft, acted upon by oil under pressure. To avoid vibration the rotor and its cell are carefully balanced, and the bearings are provided with a special damping device. A solid steel casing protects the observer and instruments in case of failure of the rotor material (figure 5).

The methods of observation used so far are based on either the absorption or the refraction of a beam of light passed through the rotating cell. The former is more direct and easier to understand, the latter more precise (figures 2 and 3).

In the former case each molecular species shows up as a step on the curve, in the latter as a peak. By such methods the molecular composition of a solution can be studied. If only a few molecular species are present, each of them of definite mass and shape, the analysis is comparatively easy. This is the case with many of the native proteins. Other substances of high molecular weight, such as the polysaccharides, consist mostly of molecules of continuously varying size. In the sedimentation diagram this shows up as a marked broadening of the peak (figure 4).

There is always a certain degree of broadening due to the diffusion or thermal motion of the molecules, but it is much slower in the case of large molecules such as those of cellulose. For comparison with the sedimentation peaks, a pure diffusion peak resulting from the blurring of a

boundary between a solution of cellulose and pure solvent is shown in figure 6.

The time required for the broadening was here fifty hours, while in the case of sedimentation broadening due to the unequal size of the molecules the time was only fifty minutes.

The unequal size of the molecules—the so-called polydispersity—shows up in the diffusion curve in a peculiar way. For a solution containing only one molecular species the broadening of the curve follows the simple statistical laws. In the case of a mixture, however, there is a marked deviation (see figure 6). As a comparison, figure 7 gives the diffusion diagram for a monodisperse substance, serum albumin, and figure 8 the sedimentation diagram for the same molecules. Here the broadening of the sedimentation peak is entirely due to diffusion, and the diffusion follows the simple statistical laws. The molecular weight can be calculated from sedimentation and diffusion according to the formula:

$$M = RTs/\{D(1 - V\rho)\}$$

where M = molecular (or particle) weight,
R = gas constant,
T = absolute temperature,
s = sedimentation constant,
D = diffusion constant,
V = partial specific volume of solute,
ρ = density of solution.

As already mentioned, the combined result of sedimentation and diffusion finally leads to a steady state, the so-called sedimentation equilibrium. The number of molecules per unit volume decreases exponentially in the direction of diminishing force. Thus the density of the atmosphere around the earth falls to half its ground-level value at an altitude of about 6,000 metres, while for a serum albumin solution exposed to a centrifugal field 10,000 times the force of gravity the corresponding distance is only 1 mm.

Owing to the fact that sedimentation equilibrium is dependent upon both sedimentation and diffusion, the molecular weights can be found directly from such determinations by means of the formula:

$$M = \frac{2RT \,.\, log(c_2/c_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)}$$

where c_1 and c_2 are the concentrations at the distances x_1 and x_2 and ω is the angular velocity.

The measurement of molecular sedimentation by means of the ultracentrifuge has proved a very useful analytical tool in many branches of science, medicine, and industry.

The blood of all vertebrates and many invertebrates contains a variety of respiratory pigments, either enclosed in corpuscles or simply dissolved in the blood-fluid. The bluish haemocyanins of the snails and crustaceans have molecular weights of the order of millions. Many of these types of molecule undergo dissociation reactions when the environment is changed, resulting in a splitting of the molecule. The reactions are often characteristic of the genus and species.

Thus the haemocyanin in the blood of the snails *Helix* is stable only within a certain *p*H range. Outside this region the molecule is dissociated into well-defined cleavage products with molecular weights one-half and one-eighth that of the original molecule. The parts have the same length as the parent molecule. The haemocyanin of *Helix pomatia* can also be split by the addition of salt. Curiously enough, only three-quarters of the molecules present are sensitive to salt; the rest remain undissociated. Evidently there are two chemically different kinds of haemocyanin molecules present in the blood of *H. pomatia*: one is split both by *p*H change and addition of salt, the other by *p*H change only.

There is a second type of snail haemocyanin which is split by a change in *p*H but not by salt (example: *Paludina vivipara*), and a third type which is split only at extremely low and extremely high *p*H values and not by salt (example: *Buccinum undatum*).

The origin of the lowest class of the vertebrates possessing red corpuscles, the *Cyclostomata* (lamprey and hagfish) has long been a question of controversy among taxonomists. The opinion now generally accepted looks upon these worm-like fishes as belonging to a very ancient side branch on the genealogical tree of the vertebrates, far removed from other living animals. The determination of the molecular weight of the red blood-pigment for the various groups of vertebrates by means of the ultracentrifuge gave the result that all vertebrates, including the different types of fish, with the exception of the *Cyclostomata*, show a value of about 69,000; the *Cyclostomata*, however, give a value of only one-fourth of this, or 17,500. Sedimentation analysis, therefore, strongly supports the result arrived at from morphological, anatomical, and palaeontological indications. To put it crudely, man is more closely related to the salmon than the salmon is to the lamprey.

Many other instances of the use of molecular sedimentation analysis in taxonomy could be given, but only one more, from the field of botany,

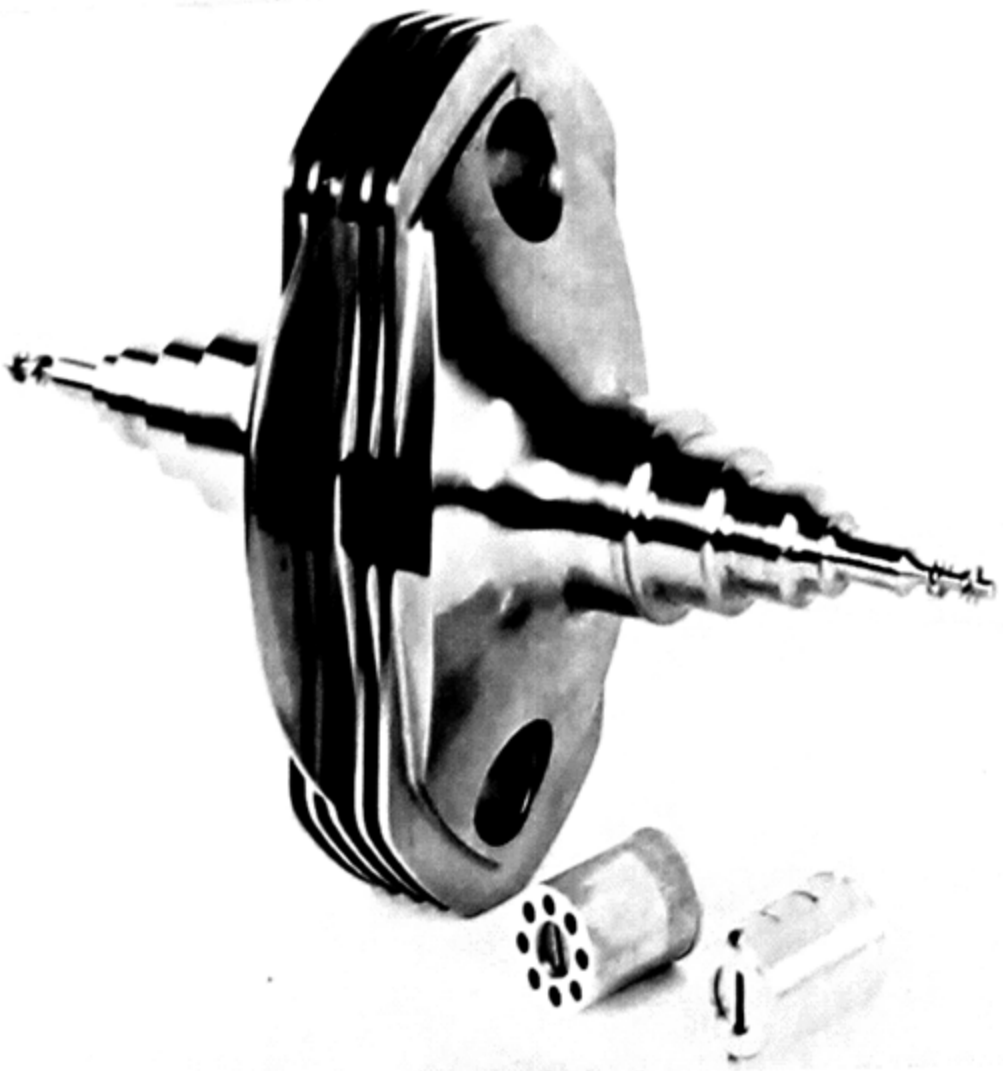


FIGURE 1 – *Rotor and cell for the oil-turbine ultracentrifuge. Beside the solution cell to the right is shown a cell for static and dynamic balancing.*

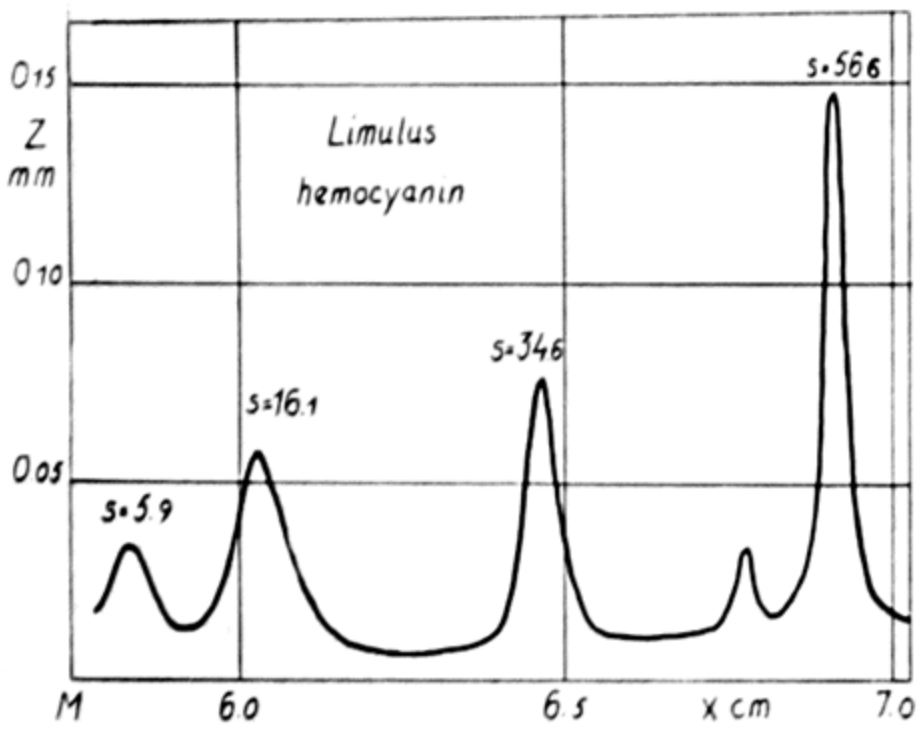
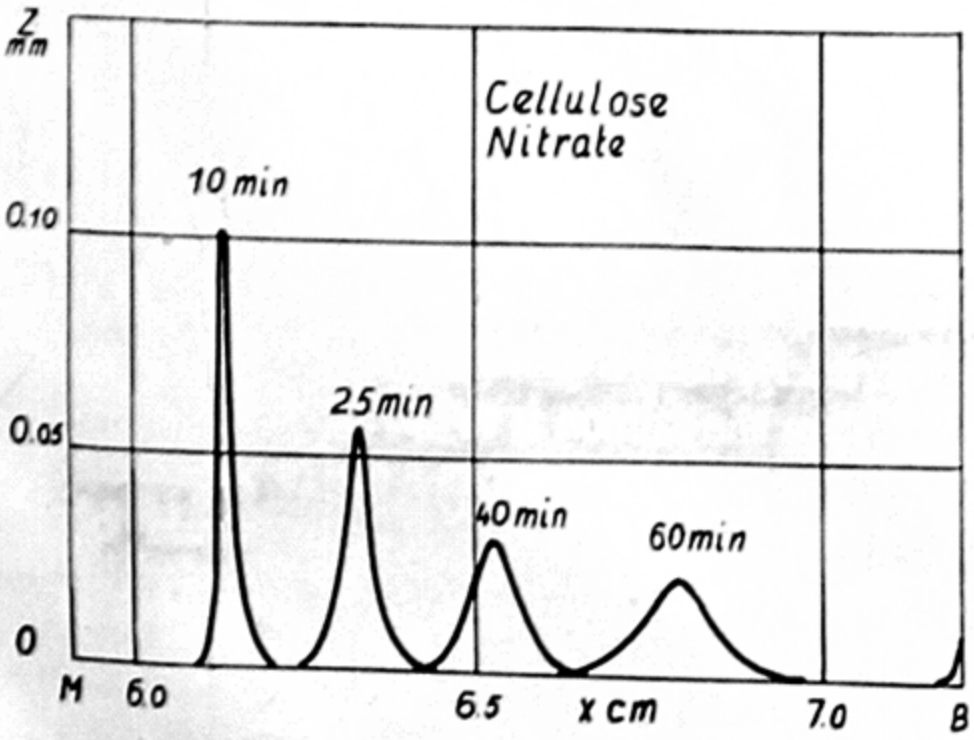


FIGURE 3 – *Sedimentation diagram of the same object taken by means of one of the refractive index methods.*

FIGURE 4 – *Sedimentation diagram of cellulose nitrate dissolved in acetone. (The cellulose used was a precipitated fraction of wood cellulose.)*



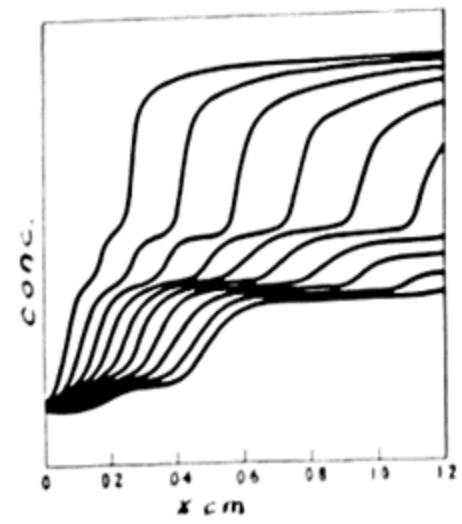
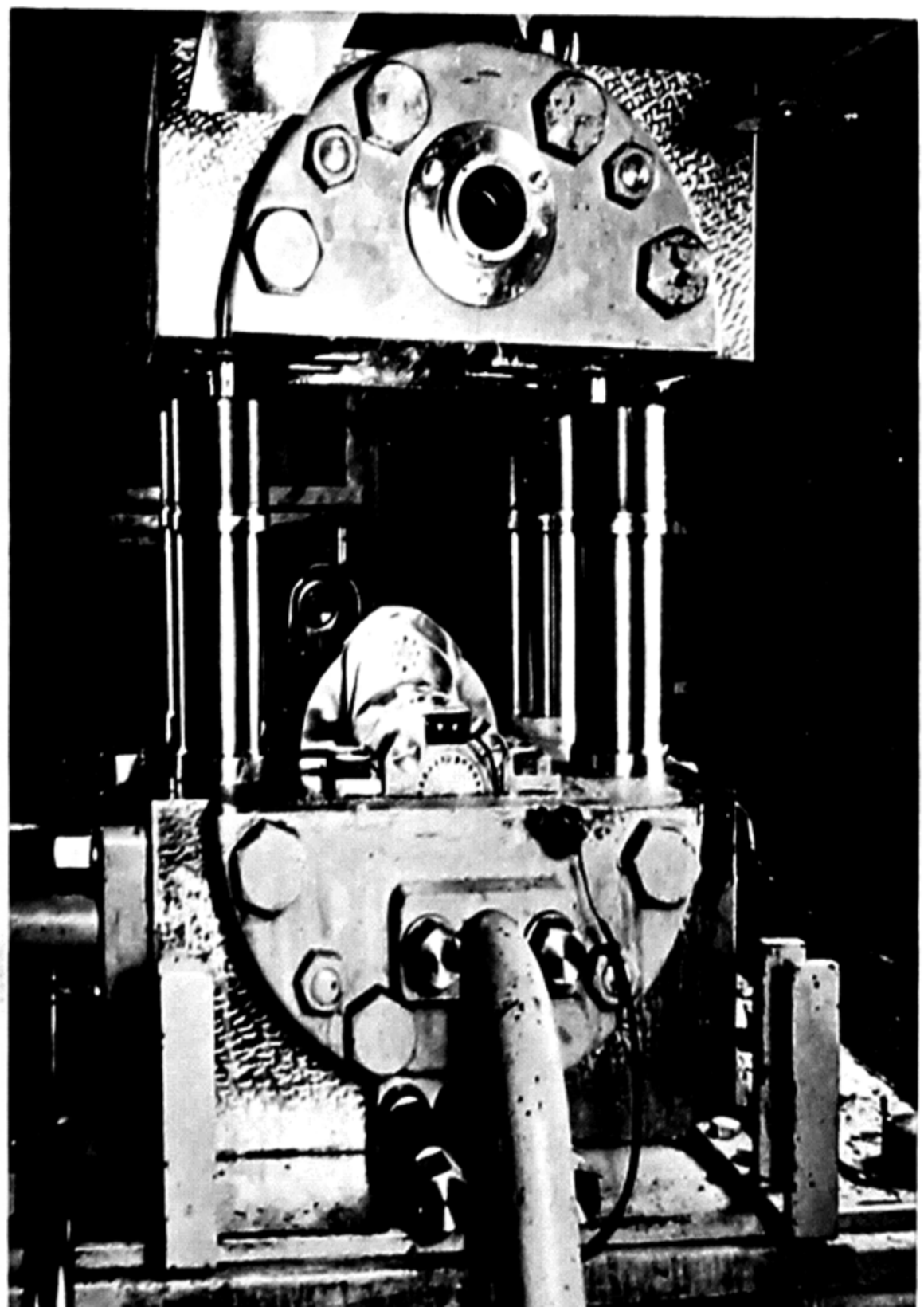




FIGURE 2 – *Sedimentation diagram of the protein molecules in the blood of the horse-shoe crab,* Limulus polyphemus, *taken by means of the light-absorption method.*

FIGURE 5 – *View of ultracentrifuge, showing the rotor in position and the heavy steel lid raised above the bolts which serve to hold the parts together.*



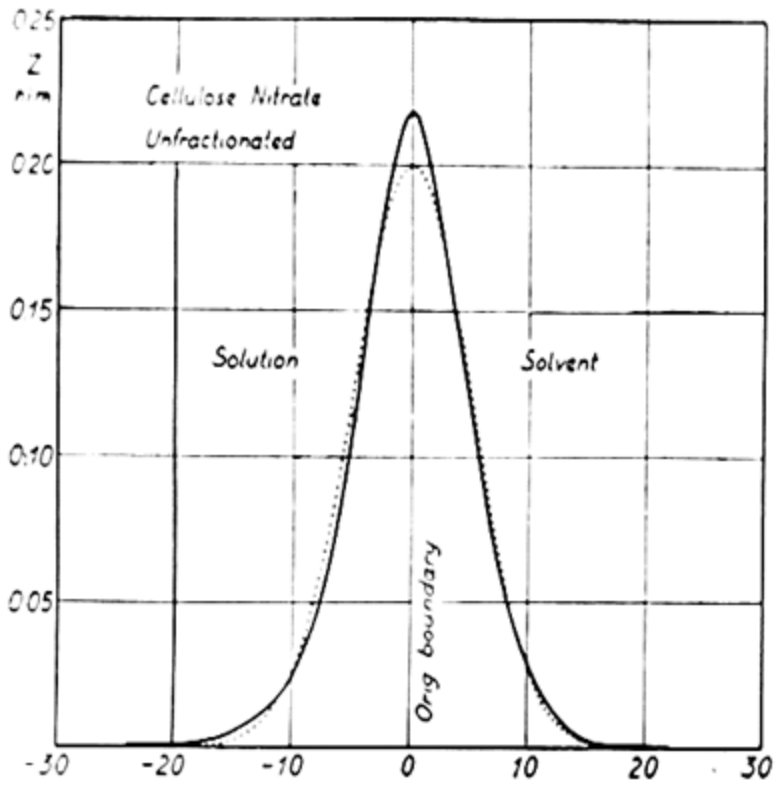


FIGURE 6 – *Diffusion diagram of cellulose nitrate dissolved in acetone. (An unfractionated sample of cellulose was used.)*

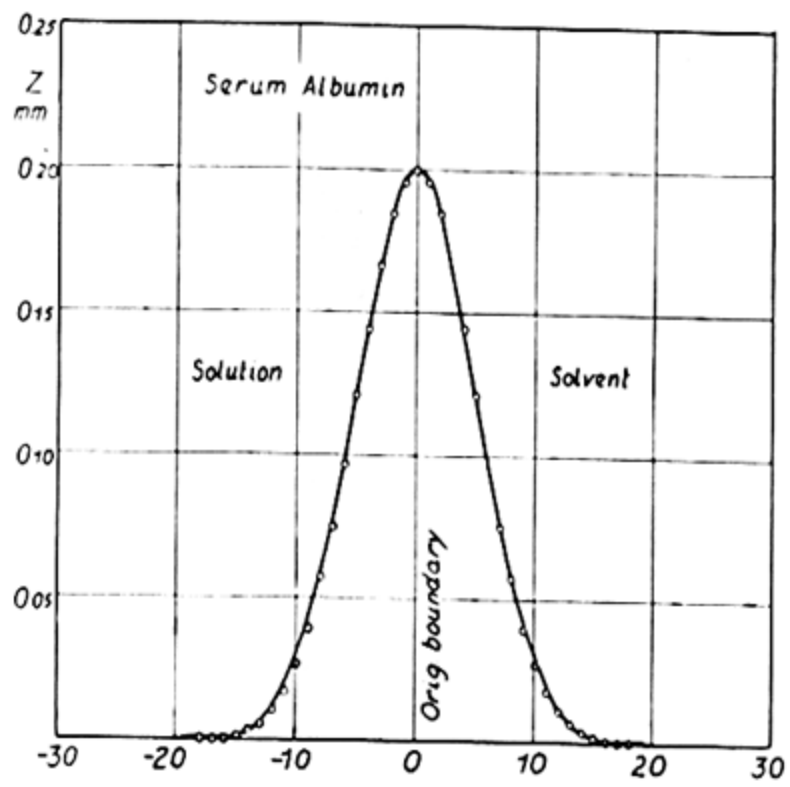


FIGURE 7 – *Diffusion diagram of serum albumin.*

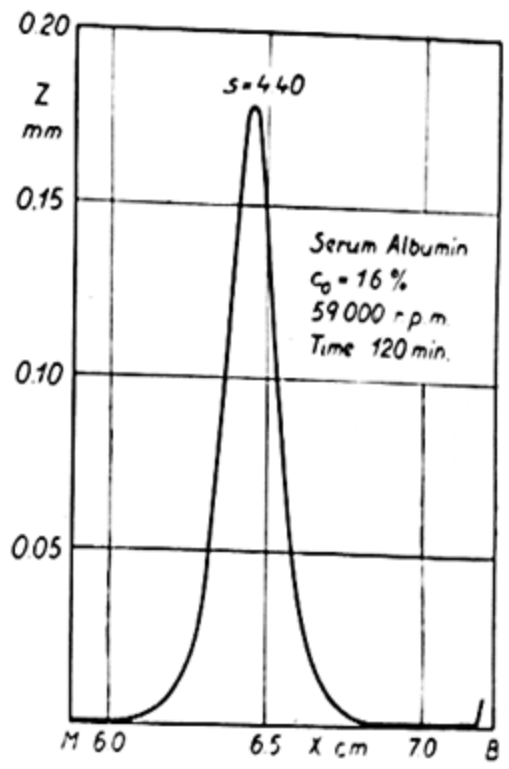


FIGURE 8 – *Sedimentation diagram of serum albumin.*

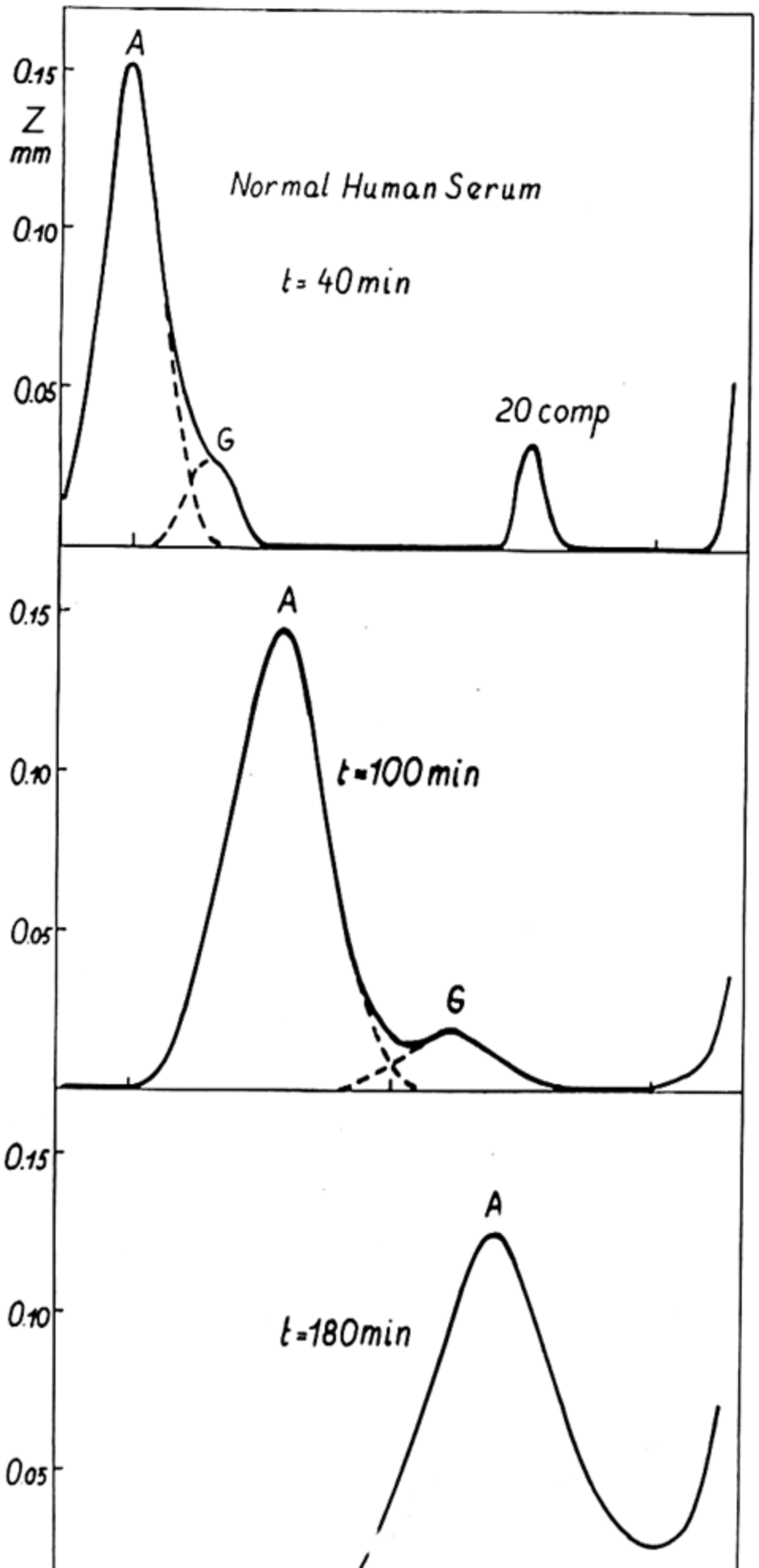


FIGURE 9 – *Sedimentation diagram of normal human serum, showing three peaks (A, G, and 20-comp.).* *See page 93.*

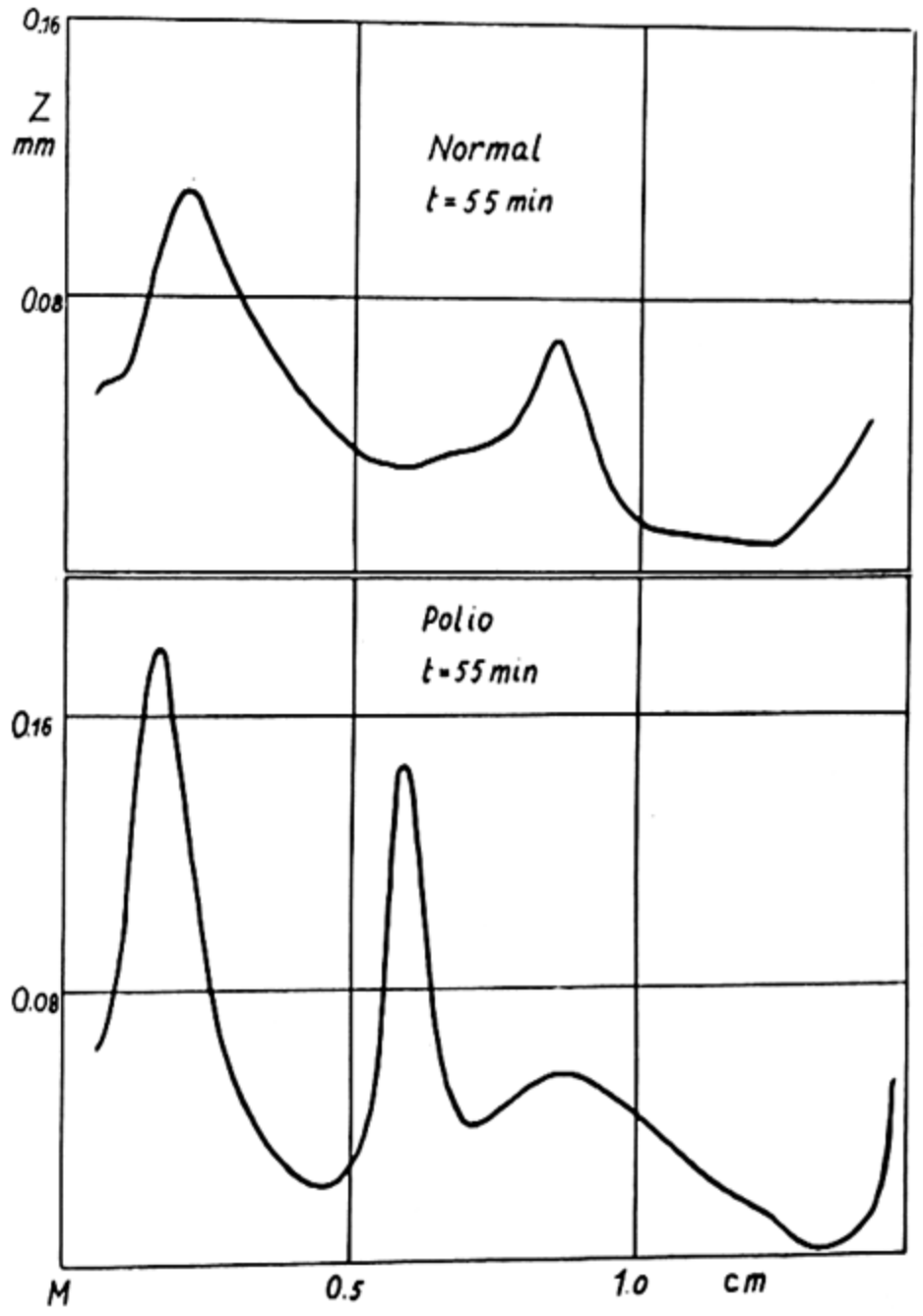


FIGURE 10 – *Sedimentation diagrams of brain extract containing poliomyelitis virus and other high-molecular proteins and of virus-free brain extract.*

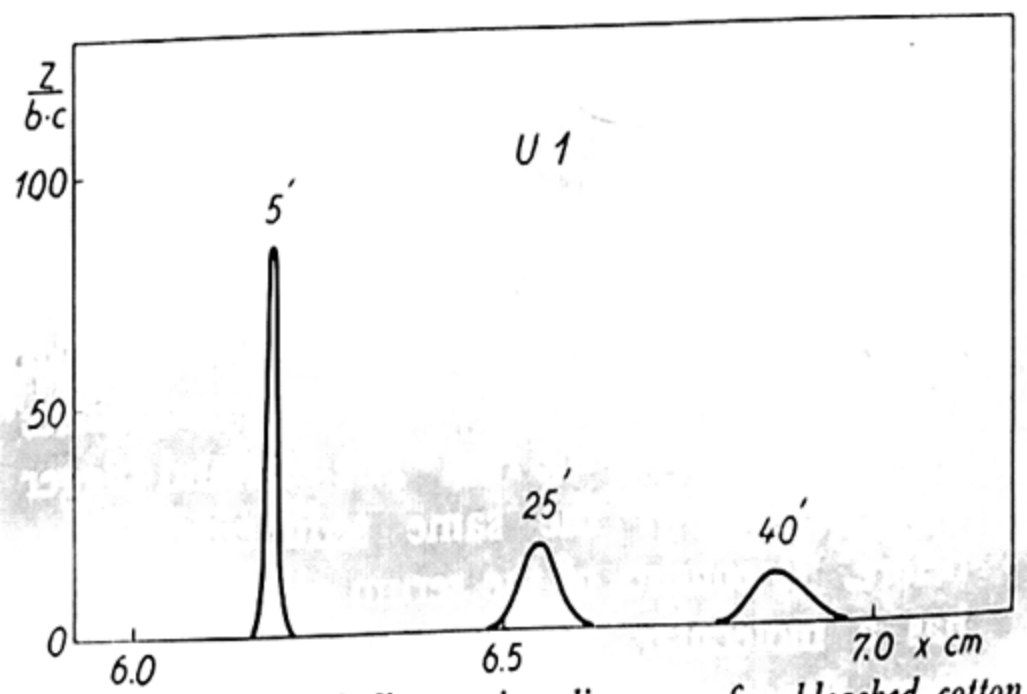


FIGURE 11 – *Sedimentation diagram of unbleached cotton linters which have been nitrated and dissolved in acetone. The molecular weight (m.w.) is 1·9 millions, corresponding to a degree of polymerization (d.p.) of 6,000.*

will be cited here. The sap in the bulbs of the *Liliiflorae* contains polysaccharides and sometimes also proteins in solution. An ultracentrifugal investigation gave the following result. Among the species of the same genus there is a pronounced similarity with regard to the material of high molecular weight. The *Lilium* species, for instance, contain a large amount of polysaccharide, while species of *Fritillaria* and *Tulipa*, belonging to the same subfamily as *Lilium*, contain more protein than carbohydrate and show sedimentation diagrams quite different from those of *Lilium*. There is one very interesting exception: *Fritillaria kamchatkensis*, which is closely related to the *Lilium* (and which has been placed by some taxonomists within this genus), yields a diagram of the *Lilium* type.

The medical applications of ultracentrifugal sedimentation are numerous. One of the most interesting examples is the disentanglement of the complicated protein system of the blood-plasma. Normal serum shows three boundaries (see figure 9). The first one, the so-called 20-component fraction, sediments to the bottom of the cell in about forty minutes under standard conditions (room temperature and 250,000 times gravity). In concentration it corresponds to only a few per cent. of the total protein in the serum. Its molecular weight is of the order of half a million. At the same time as the first boundary reaches the bottom of the cell, a second broad boundary has usually just separated from the top of the solution. As it moves towards the periphery it eventually splits into two boundaries. The first, and smaller, one reaches the bottom in 1½–2 hours; it has a molecular weight of 150,000–180,000, and in concentration it amounts to 10–20 per cent. of the total. Finally, the major part of the protein sediments in the last boundary, which reaches the bottom of the cell in about three hours. This boundary, however, does not correspond to a single substance, but represents a protein called β-globulin as well as the serum albumin. The composite nature of the third boundary is easily demonstrated in the case of normal human serum. If, before the run, the serum is diluted with an equal volume of 0·2 molar disodium phosphate instead of with physiological saline, the third boundary will separate into two boundaries towards the end of the run. The first and bigger boundary shows the same sedimentation as before. It consists of the serum albumin, which has a molecular weight around 70,000. The more slowly moving boundary consists mainly of β-globulin, which is a lipo-protein. The density of this protein is close to 1, whereas the density of most other proteins is about 1·3. The sedimentation of the lipo-protein is therefore much more dependent on the density of the solution than that of the other proteins. This property of the lipo-protein has been used for its separation from normal human serum.

Up to the present no other mammalian sera have been found to contain such a low-density lipo-protein as the one in human serum. There are, however, many reasons for believing that other mammalian sera also have a β-globulin which sediments with the albumin, but its lipid part has a higher density than the human one.

The general appearance of the sedimentation diagram from normal adult mammalian serum seems to be qualitatively the same for all species, but there are usually some small quantitative differences. Even the lower vertebrates seem to give qualitatively the same sedimentation diagrams as the mammals do. The *Cyclostomata*, however, have a minor component with a molecular weight of about 35,000 and a major component with a molecular weight of about 360,000.

The sedimentation diagram for a given animal is not always the same, but varies with its age. Thus the ultracentrifuge has revealed that a hitherto unknown serum protein, now called fetuin, is present in many foetal sera and in sera from newly born animals. It has a lower molecular weight (around 50,000) than any of the previously isolated serum proteins.

Antibody production during the process of immunization is often manifested in the serum diagram as an increase in either the so-called γ-globulin or in the heaviest protein component. Some diseases also produce great changes in the serum sedimentation diagrams, and it may be possible, for instance, to classify various myelomas according to the sedimentation diagrams obtained from the patient's serum.

The changes in a serum due to the increasing age of the animal may be illustrated by bovine serum. In the foetal serum diagram hardly any γ-globulin is perceptible. Besides an asymmetric peak consisting of albumin and fetuin, a small amount of a heavy component is present. A similar diagram is obtained from the serum just after birth. Some time after the calf has received colostrum, γ-globulin appears in the serum diagram. During the first weeks after birth the fetuin and the γ-globulin decrease. Later the fetuin practically disappears, whereas the γ-globulin

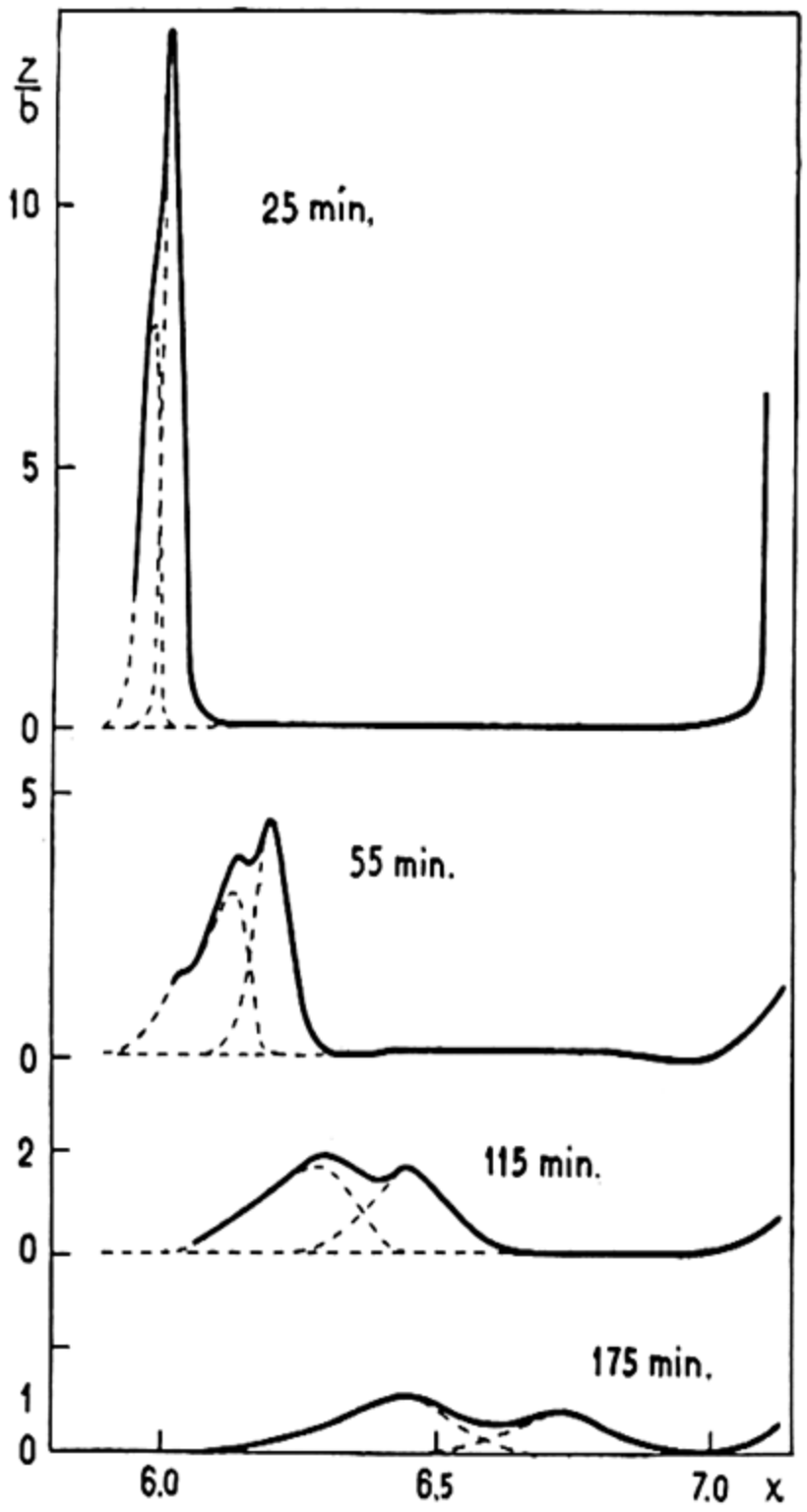


FIGURE 12 – *Sedimentation diagram of native wood cellulose obtained by extraction with cuprammonium. Two maxima are to be seen, one representing the cellulose proper (m.w. = 700,000, d.p. = 4,300) and the other wood polyoses (hemicellulose).*

organic polymers have been studied by means of ultracentrifugal sedimentation. The most important of the macromolecular carbohydrates, from a technical point of view, is cellulose. It occurs in a fairly pure state in certain fibres such as cotton and flax. Native cellulose, however, generally occurs in combination with other carbohydrates and with lignin, and its liberation requires rather drastic chemical treatment (the sulphite and sulphate processes).

For many purposes the industrially prepared cellulose should contain molecules consisting of the longest possible chains of glucose groups, and it is often considered advantageous that the length of the individual molecules should be nearly equal (monodisperse). In the industrial processes for isolating cellulose from wood a considerable degradation takes place, especially during the later stages. The chain molecules break, and shorter and more unequal (polydisperse) pieces result. It is of considerable importance to find the most favourable conditions for producing a cellulose of a specified molecular type. Investigations of this kind have been carried out by means of the ultracentrifuge. An example of a comparatively monodisperse cellulose of very long chain molecules is given in figure 11. Native wood cellulose, on the other hand, is much more polydisperse (figure 12).

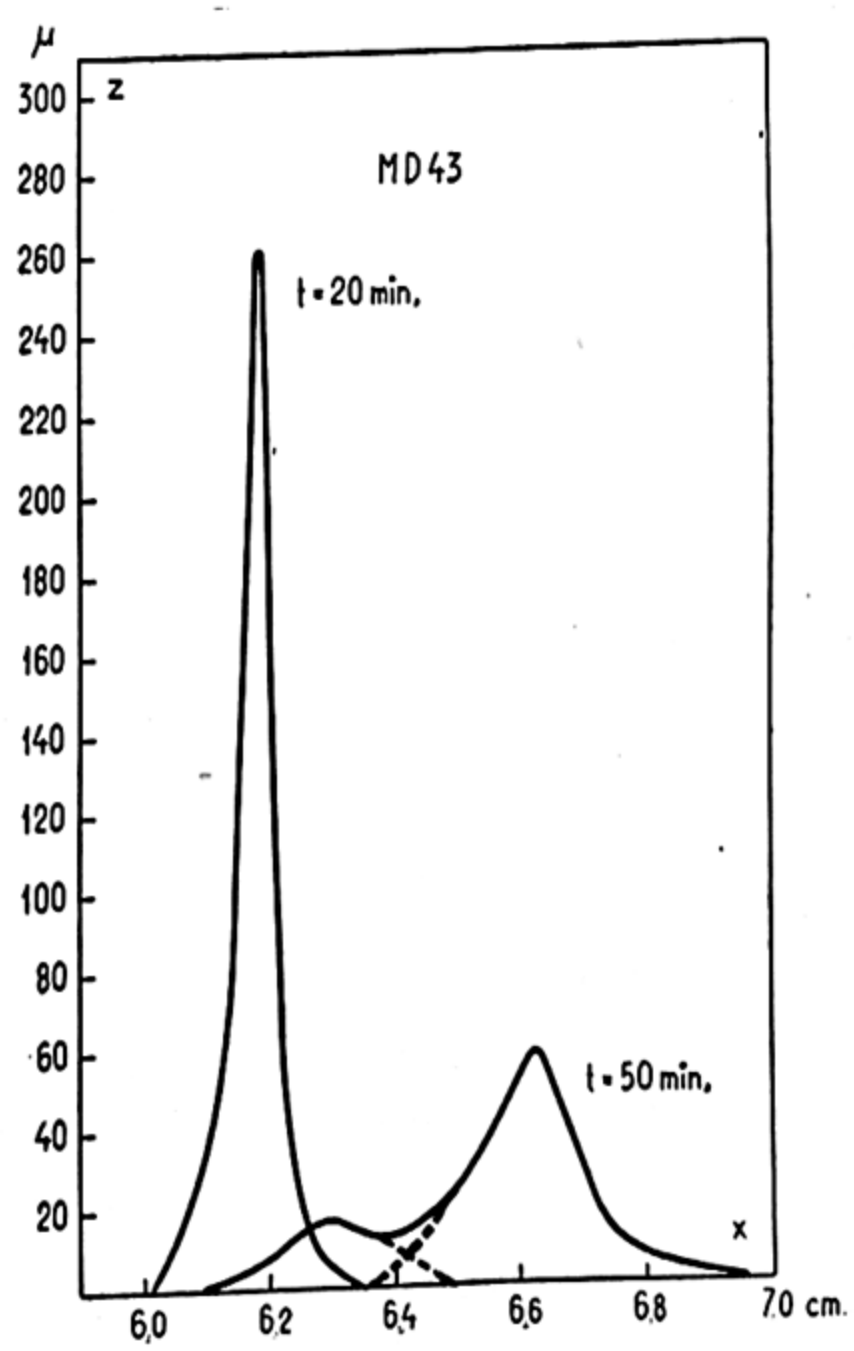


FIGURE 13 – *Sedimentation diagram of sulphite cellulose nitrated and dissolved in acetone (m.w. = 530,000, d.p. = 1,850).*

increases, when the natural immunity is being built up, until it reaches its 'natural' level.

Another medical application is in the study of viruses. Directly after the first preparation of virus crystals (tobacco mosaic) the analytical ultracentrifuge was used for the determination of the mass of these huge molecules and to compare various strains of virus. A great number of such determinations have been made during the last ten years.

Sedimentation measurements in the ultracentrifuge have proved very useful as a means of following the process of purification of a virus. As an example, the isolation of poliomyelitis virus from brain tissue or intestinal contents may be mentioned. In figure 10 are given the sedimentation diagram of brain extract containing both virus and other high-molecular proteins (three peaks), as well as a control diagram of the virus-free brain extract.

Many industrial problems concerning material of high molecular weight belonging to the polysaccharides and to various groups of synthetic

Industrial wood cellulose manufactured according to the sulphite process is broken down considerably, and the amount of wood polyoses is diminished (figure 13).

In such cases as cellulose, where the broadening of the sedimentation curves is caused entirely by the different rate of sedimentation of the individual molecules, a measure of the polydispersity is obtained by calculating dB/dx, the rate of broadening with increasing distance from the centre of rotation (cf. figure 4).

The complete description of a polydisperse material such as cellulose requires the determination of the distribution or frequency curve for the weights of the molecules. This problem is very difficult, and so far only approximate solutions have been found. In figure 14 are given the frequency curves for two commercial cellulose materials, computed from sedimentation data.

Among the synthetic high polymers and their natural prototypes rubber plays an important role. The technical value of various types of rubber depends to a considerable extent upon the size and shape of the molecules. Here sedimentation analysis in the ultracentrifuge has furnished valuable information. In the case of neoprene it was found that bulk polymerization gives molecules of simple chain type, while certain kinds of emulsion polymerization produce molecules of a more branched type. For most purposes it is desirable to obtain a rubber with simple chains, and therefore the polymerization process should be conducted in such a way as to yield that type of molecule. Also in the case of plastics, such as polystyrene, methyl methacrylate, and other polyethylenes, the ultracentrifuge has been used for the control of industrial processes.

Above I have tried to indicate how by means

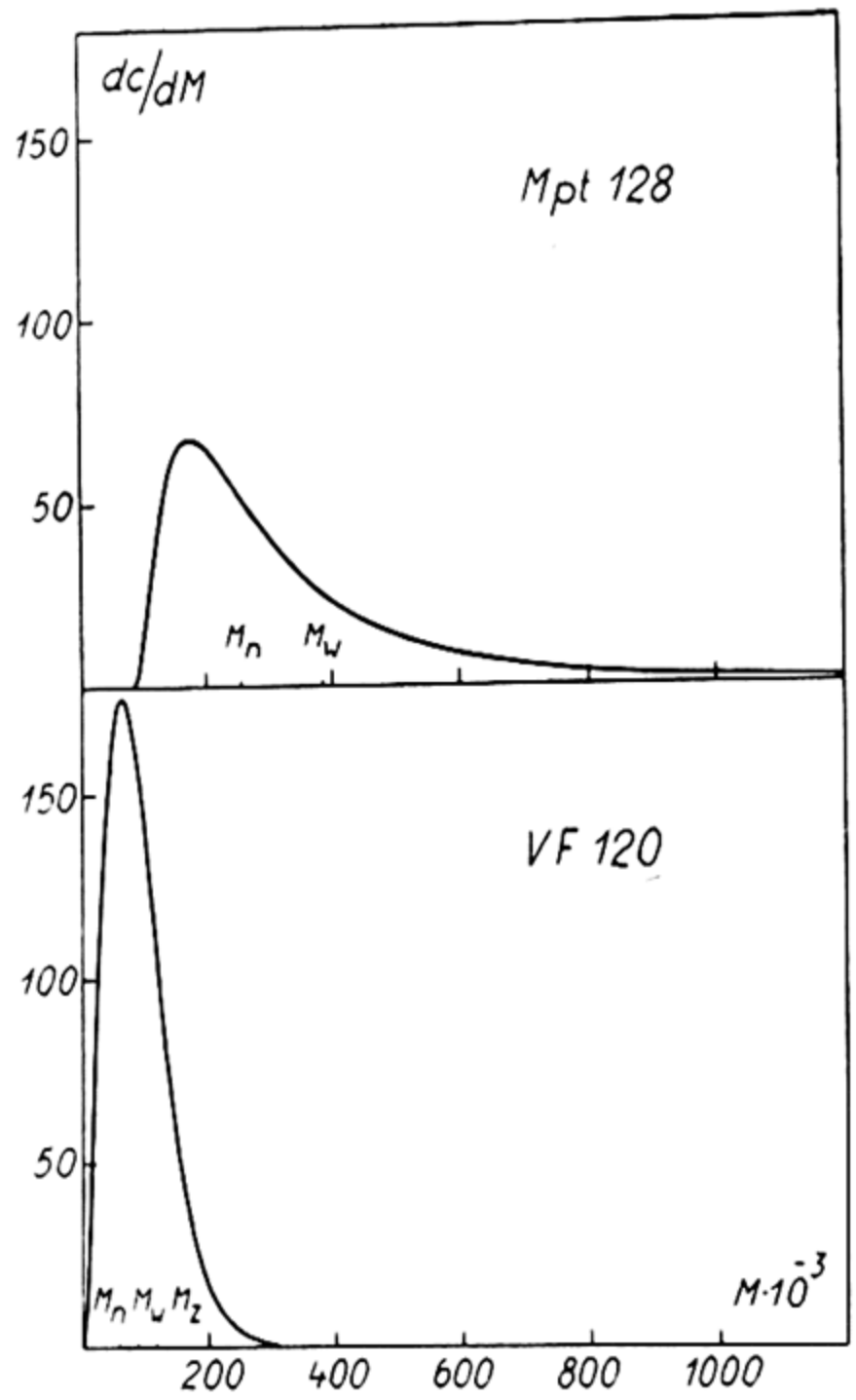


FIGURE 14 – *Frequency curves for two different cellulose materials nitrated and dissolved in acetone.*

of studying molecular sedimentation we have been able to collect a wealth of facts concerning material of high molecular weight, both native substances built up within the living organism such as proteins and carbohydrates, and artificially produced macromolecular substances such as plastics. The ultracentrifugal method is, however, by no means the only one for the study of these problems. There are also electron microscopy, X-ray analytical methods, osmotic methods, diffusion measurements, viscosity methods, and so on.

Book reviews

ODYSSEY OF A BOTANIST

A Botanist in Southern Africa, *by John Hutchinson. Pp. xii + 686, with numerous photographs, drawings, and maps. P. R. Gawthorn Limited, London.* 1946. 45*s. net.*

This is a fine book, and one cannot do justice to it in a short review. The illustrations alone are a remarkable contribution to botanical literature, including numerous line drawings of living South African plants in Dr Hutchinson's well-known and most attractive style; a superb series of photographs which show many of the plants growing in their natural habitats; and various maps showing geographical distribution. The text takes the form of an account of the various journeys made by Dr Hutchinson and his companions, and of the plants which they encountered. There are sections on the floral regions of South Africa, the history of botanical exploration in the country, and allied matters, so that the book has the double value of a travel story and a student's handbook. There is a foreword by General Smuts, who figures largely in the book and who in fact made much of the work possible. The whole production is a monument to Dr Hutchinson's energy, botanical insight, and artistic skill; to the enterprise of Messrs Gawthorn, who published, at a very difficult time, an expensive book of a type which is too rarely seen in this country; and to the public spirit of General Smuts and other South African botanists.

T. A. STEPHENSON

A HISTORY OF CHEMISTRY

Die Entwicklungsgeschichte der Chemie, *by H. E. Fierz-David. Pp.* 425. *Verlag Birkhäuser, Basel.* 1945. 21.50 *Swiss francs.*

This attractive book, with over a hundred illustrations, including portraits and reproductions from old books, is not a formal history of chemistry but is intended to interest and instruct chemists who have no opportunity of studying original sources. It deals with the origins of chemistry, alchemy, the period from Boyle to Lavoisier, the atomic and molecular theories, and the development of pure and applied chemistry in the nineteenth century. The author explains that he has not used original sources but has drawn his material from books, and in some cases he does not seem to have made use of more recent publications which would have been helpful to him. The collection of miscellaneous book titles in the appendix serves no useful purpose, and could have been replaced by a list of books on the history of chemistry which would have supplied the many gaps in the story now presented. Although the text is generally accurate and informative, there are lapses, as when Faraday is put before Berzelius in the development of the electrochemical theory, and in the account of the theory of valency Frankland is not mentioned. The author has managed to cover a large field in an interesting manner, and all chemists who read German will find the book attractive. To the historian of chemistry it will be less useful, but the author does not claim to have had his requirements in mind. The references, however, will disclose some interesting features even to the expert, and the book is one which should find its place in the field of historical works.

J. R. PARTINGTON

PHYSICS AND PHILOSOPHY

Fundamental Theory, *by Sir A. S. Eddington. Pp. viii* + 292. *University Press, Cambridge.* 1946. 25*s. net.*

There will be few (and an experimental physicist cannot be expected to be among them) who will be able to understand in full detail all the profound and subtle arguments developed in this remarkable posthumous treatise on the fundamental particles and constants of nature, which is edited by Sir Edmund Whittaker. Eddington investigates the way in which structures are related to the uncertainty constant of the frame of reference, and already by page 10 obtains a simple relation between the range constant of nuclear force and the speed of recession of nebulae, thus straddling physical concepts from the atomic nucleus to the cosmos.

The book is rich in brilliant analogy and is enlivened by unexpected flashes of humour, despite its profundity. Important concepts developed include the replacement of gravitation by a 'mechanical' exclusion principle corresponding to the 'electrical' exclusion principle of Pauli. Eddington's now well-known epistemological theory for the number of particles in the universe is linked up with the general derivation of atomic constants. By adopting experimental values for three natural constants other atomic constants can be obtained, the agreement with observation being startling. To select two examples only, (*a*) fine structure constant; observed = 137·009, theoretical = 137; (*b*) ratio of masses proton/electron; observed = 1,836·27, theoretical = 1,836·34. The theory, among other matters, also predicts the existence of mesotrons of respectively 174 electron masses and 2·38 proton masses.

Only time can decide the ultimate importance of this outstanding contribution to physics and philosophy.

S. TOLANSKY

FREE RADICALS

The Chemistry of Free Radicals, *by W. A. Waters. Pp. viii* + 295. *The Clarendon Press, Oxford.* 1946. 20*s. net.*

Free radicals were at one time little more than chemical curiosities, yet the essential part which they play in many of the familiar reactions of organic chemistry can be judged by the very wide scope of this book, which appears at a most opportune moment. It is still possible in a single volume to give a comprehensive account of this rapidly expanding subject. Some of the earlier ground is well known, e.g. the discovery and properties of the radicals of the triphenylmethyl and diphenyl nitrogen types.

Chapters in the book are devoted to the parts played by free atoms of hydrogen, oxygen, chlorine, and sodium in gaseous reactions and photochemical decompositions. The author deals also with reactions which are catalysed by free radicals, including halogen atoms, peroxide catalysed reactions, and the chain polymerization of olefines. Of particular interest are the chapters dealing with free alkyl radicals and their reactions in solution, and with the production and properties of the free aryl radicals generated in solution by the decomposition of diazo compounds, to our knowledge of which the author has himself made outstanding contributions. The final chapters deal with reactions involving metals as free radicals, oxidation processes, and some possible applications of free radical chemistry to biochemical processes.

W. BAKER

RELAXATION METHODS

Relaxation Methods in Theoretical Physics, *by R. V. Southwell. Pp. vi* + 248. *Oxford University Press, London.* 1946. 20*s.* net.

Interest in relaxation methods for use in design and research is steadily growing as their power and range become more widely known. Many will be glad that, in addition to developing the methods, the author has taken the trouble to write a connected account of them for those who wish to understand, and even more for those who wish to use, them. Space forbids a description of the methods, but numerical solutions to a wide variety of problem, some of which still defy 'orthodox' analysis, are obtained, and are exhibited very clearly and with considerable detail in a series of diagrams. In each of the thirty-five specific problems solved the 'background' is skilfully summarized before computational details are given, so that the reader has a complete 'case-history' to enable him to treat with confidence and understanding similar problems which he may encounter. The author is to be congratulated upon an exposition orderly, lucid, and detailed, and the publishers upon the production of a very handsome volume at a very reasonable price. Nor must some credit be withheld from the research team, without whom, as the author generously admits, such a striking set of results could hardly have been obtained.

W. G. BICKLEY

ENDEAVOUR

A quarterly review designed to record the progress
of the sciences in the service of mankind

VOLUME VI JULY 1947 NUMBER 23

Louis Pasteur

The fiftieth anniversary of the death of Louis Pasteur fell on 28th September, 1945, but at that time scientists of the world were too preoccupied with the immense task of reorganizing their work after six years of war to mark the occasion with the ceremony it deserved. Although Pasteur's researches were to a great extent in the fields of medicine and biology he was first and foremost a chemist and made many notable chemical discoveries, especially in the field of stereochemistry. His successes in biology and medicine were due in large measure to his application of chemical methods to these branches of science—a task which an earlier great French chemist, Lavoisier, would doubtless have essayed but for his untimely death. The present is a particularly appropriate time to recall Pasteur's life and work, for the centenary celebrations of The Chemical Society and the Eleventh International Congress of Pure and Applied Chemistry have at this time brought to London the greatest gathering of chemists that the world has ever seen.

Louis Pasteur was born at Dôle (Jura) on 27th December, 1822. His father was a tanner, who, appreciating the value of education, sent his son to be educated at Besançon, and in 1843 Pasteur was admitted to the *École Normale* in Paris. It was while working as an assistant in the laboratory of A. J. Balard at the *École Normale* that he made the fundamental discovery of molecular asymmetry, in 1848. In the same year he went to Dijon, and soon afterwards to Strasbourg, as a teacher. In 1854 he became professor and dean of the faculty of sciences at Lille, and in 1857 he returned to the *École Normale*, as director of scientific studies.

When he began his observations on tartrates in 1847, it was known that certain organic compounds in the liquid or dissolved state were capable of rotating the plane of polarization of polarized light, but no satisfactory explanation of the phenomenon had been advanced. Pasteur not only showed that the effect on polarized light was due to asymmetry of molecular architecture, but devised methods of resolving racemic mixtures. Indeed, his three methods of resolution—mechanical separation, separation by selective fermentation, and separation of derivatives formed with optically active reagents—are still, a century later, the only general methods available to chemists. For this brilliant work, by virtue of which he takes rank as the founder of stereochemistry, Pasteur was awarded the Rumford Medal of the Royal Society in 1856. In France, however, his first presentation as a candidate for the *Académie des Sciences* was unsuccessful, and his election was delayed until 1862.

At Lille, Pasteur's attention was attracted to the application of fermentation in the production of alcohol from grain and beet-sugar. He was thus led on to study the souring of beer, and in 1864 he extended his inquiries to the cause of sourness, bitterness, and ropiness in the celebrated rosy and tawny wines of his native Arbois. He examined under his microscope the micro-organisms present in good beer, and compared them with those of sour beer. In both he found yeast cells, but in the sour beer he found also other cells which on investigation proved to be responsible for the unpleasant taste. He showed that the growth of these harmful organisms could be inhibited by gentle heat, and thus introduced the process which we now call pasteurization. The application of pasteurization to milk has since become, as everyone knows, one of the principal methods of preventing the spread of tuberculosis. Pasteur also studied the process of vinegar-making and was able to suggest valuable improvements in this important industry.

Among the far-reaching results of Pasteur's

biochemical work was his conclusive demonstration of the falsity of the theory of spontaneous generation, at that time still widely accepted. Somewhat surprisingly, Pasteur found his conclusions challenged, but he soon enlisted able supporters in Joseph Lister—who quickly perceived the great significance of Pasteur's work in his own field—and John Tyndall, the physicist. The Royal Society reaffirmed its confidence in him by electing him to membership in 1869 and awarding him the Copley Medal in 1874. The opposition eventually proved of value, however, for it led Pasteur to make new experiments, which so fully supported his earlier conclusions that they eventually proved unassailable.

From the study of micro-organisms which bring about the fermentation of wines and beers, Pasteur was led to the discovery of the bacterial causes of disease. This phase of his work began with his election to the *Académie de Médecine* in 1873. His candidature was opposed, and was approved by a majority of only one. Nevertheless, within ten years his work had introduced entirely new conceptions of the origin of certain diseases. In the years 1877–81 he made swift progress in this field. Much of his earlier experimental work (1865–8) was done with silkworms, for at that time the silk industry was in serious difficulties owing to the incidence of diseases which were destroying tens of thousands of the grubs. His work not only established his general theories but proved of immense practical value to the silk industry. From the diseases of silkworms he went on to the study of infectious diseases in general, and characterized many of the more important pathogenic bacteria. He discovered, too, the principles of inoculation by the use of attenuated strains of bacteria, thus placing the earlier work of Jenner on a logical basis. In this field his work on rabies, anthrax, and chicken cholera is particularly noteworthy. In 1881 he accepted a challenge to stage a public demonstration of his methods of immunizing cattle against anthrax. The demonstration, carried out before a large gathering of distinguished men, was wholly successful and did much to establish general acceptance of his views. It is impossible to compute the number of lives that have been saved by the general introduction of the principles of vaccination into medicine.

Not until 1887, however, was the controversy which had raged about Pasteur's work completely stilled. In the previous year the British Government had appointed a commission—which included James Paget, Joseph Lister, and Henry Roscoe—to study Pasteur's method for the treatment of rabies. In July 1887 they published a report substantiating every claim that Pasteur had made. A few days later he deposited a copy of the report at the offices of the *Académie des Sciences* in Paris. Of this event he said: 'During the long course of my scientific career I have never experienced a happiness equal to that which I felt on reading this report.'

Pasteur's work is notable for the breadth of understanding which he displayed in the study of widely differing phenomena. Any one of his great discoveries—in stereochemistry, in fermentation, or in bacteriology—would have assured him undying fame. Yet the validity of some of his work was questioned in France, and he was faced at times with violent opposition. That one man should have made so many brilliant discoveries, and despite bitter criticism, is truly amazing. His success, as already remarked, may be attributed in part to his pioneer use of chemical methods in the study of biological problems. He was entering an almost untouched field, and with so powerful a tool was able to reap a great and immediate harvest. His successors in the field of biological chemistry have made equally great discoveries, but few individual efforts have been comparable with his. 'Let us all work,' wrote Pasteur; 'that only is enjoyable.'

In 1887 subscriptions were invited for the building of a research institute in which Pasteur could worthily continue his work. There was an immediate response from all over the world, and on 14th November, 1888, the Pasteur Institute was opened in Paris. Today this building and other Pasteur Institutes in many different parts of the world form a fitting memorial to him and his achievements.

Editor: E. J. HOLMYARD, M.A., M.Sc., D.Litt., F.R.I.C.
Deputy Editor: TREVOR I. WILLIAMS, B.A., B.Sc., D.Phil.
Foreign Editor: J. A. WILCKEN, B.Sc., Ph.D.

Imperial Chemical Industries, Nobel House, Buckingham Gate, London, S.W.1.

The age of the earth

ARTHUR HOLMES

The history of the many efforts that have been made to discover the age of the earth's crust reveals a remarkable alternation of contrasted estimates—long and short. Kelvin applied a corrective by insisting that the time that has elapsed since the earth consolidated sets an upper limit to the duration of geological history. Professor Holmes here describes the latest refinement in methods based upon the detailed study of radioactive minerals, and concludes that from the data at present available the most probable estimate is 3,350 million years.

Long before it became a scientific aspiration to estimate the age of the earth's crust, many elaborate systems of world chronology had been devised by the sages of antiquity. The most remarkable of these occult time-scales is that of the ancient Hindus, who calculated that it is now (A.D. 1947) 1,972,949,048 years since the earth came into existence. By a curious coincidence this characteristically precise assessment is of the same order as the 2,000 million years which has recently been the most widely favoured estimate for the age of the expanding universe.

If geological concepts had developed in a community endowed in advance with so generous a concept of the past, much confusion and bitter controversy might have been avoided. But in western Europe the age of the earth had long been identified—to within a few days—with the few thousand years of mankind's history as recorded in the narratives of the Old Testament. On the interpretation of Archbishop Ussher (1581–1656), the creation of the world took place in the year 4004 B.C., and pioneer geologists whose observations suggested that the Mosaic traditions might not be scientifically reliable were branded as dangerous heretics.

A mild though significant instance of the prejudicial influence of this cramping limitation of time is afforded by a remark made by the renowned astronomer Edmund Halley (1656–1742) in the course of a communication to the Royal Society on a *Proposal . . . to discover the Age of the World* (1715). Halley realized that the sea had become salt because of the accumulation of saline material contributed by inflowing rivers, and he suggested that the total amount of salt in the sea might therefore provide a measure of the age of the oceans. At that time the necessary data for making the calculation were not available, and Halley lamented that the ancient Greek and Latin authors had not 'delivered down to us the degree of the saltness of the sea, as it was about 2,000 years ago; for then,' he continued, 'it can not be doubted but that the difference between what is now found and what was then, would become very sensible.' Now obviously, if Halley had been thinking in millions of years instead of thousands, he must have realized that the increase of salinity since Greek or Roman times would be quite undetectable. Nevertheless, he did not fail to express his suspicion that 'the world may be found much older than many have hitherto imagined.' It was James Hutton (1726–97) (see page 109) who first clearly grasped the full significance and immensity of geological time.

Today we know that the earth's history has included a succession of at least ten major cycles, each involving (1) thick accumulations of sediments and volcanic rocks in a subsiding belt of the crust; (2) intense compression of the belt, resulting in folding and crumpling, and accompanied by metamorphism of the deeper rocks and the formation of great masses of granite; and (3) general uplift of the belt and the wearing away of its exposed portions by denudation. The effects of such changes are illustrated in figures 1 and 2. The Alps and the Himalayas are examples of mountain systems now in stage (3) of the latest of these mountain-building or 'orogenic' cycles, as they are called. The rocks of Cornwall and Devon are relics of the immediately preceding cycle, and those of the Lake District and most of Scotland and Wales and Norway belong to the next earlier one. From beneath the North-West Highlands of Scotland and the mountains of Scandinavia the rocks of even older cycles appear (figure 3). So, going farther afield than Hutton did, we can travel back through a long series of these contorted records of earth history. But however far we penetrate into the past we still, like Hutton, find 'no vestige of a beginning.' How this comes about can readily be grasped by reference to figure 6 (page 104). In every continent the oldest known rocks are

found to be metamorphosed sedimentary types which gradually merge into completely reorganized rocks such as granite. The granite, however, instead of being older than the rocks in which it is emplaced, is actually younger, since it crystallized in its present form during or after the folding of the pile of sediments with which it is associated. Everywhere the oldest visible rocks pass sideways or downwards into granitic foundations that are younger than themselves. But since the oldest visible rocks are of sedimentary origin, they must have been derived from rocks of still greater age: from rocks now represented by pebbles and sand grains, and of which no other recognizable trace has so far been found.

Hutton's experience covered only a small proportion of the earth's history now known to us, and he was therefore recording no more than the sober truth when he declared he could find 'no vestige of a beginning.' In the absence of guiding data, he made no attempt to estimate the rates of geological processes or the periods represented by their products. Many of his successors, however, exhilarated by their newly-found freedom, became unduly reckless in their extravagant demands for time. In 1859, for example, Darwin estimated from the supposed rate of chalk erosion in Kent that the time required for the denudation of the Weald and the recession of the bordering escarpments of the North and South Downs to their present positions was probably about 300 million years. We now know that this estimate was at least five times too long; but Jukes, commenting on it at the time, thought it quite as likely that the period required might have been a hundred times as long. Evidently 30,000 million years was not considered absurdly excessive for a small fraction of geological time.

Kelvin, one of the greatest pioneers of geophysics, then entered the field with a dramatic counterblast against the current assumptions of unlimited time. He argued that since there is a heat-flow through the earth's crust, measurable in terms of the downward increase of temperature and the thermal conductivities of rocks, the earth could be regarded as a cooling globe which must therefore have been progressively hotter in the past. Beyond the dim horizon of the oldest rocks he envisaged a 'beginning' corresponding to the time when the earth was molten and newly born from the sun. In 1862 he set himself the problem of calculating the time that had elapsed since the earth's consolidation. Because of uncertainty in many of the data, he allowed wide limits to his solution, concluding that the observed temperature gradients would have been notably lower than they are if the crust had solidified more than 400 million years ago, and notably higher than if solidification had been completed less than 20 million years ago.

Kelvin's challenge initiated one of the many scientific controversies that enlivened Victorian times. Despite many protests, however, he finally narrowed his limits to 20 and 40 million years (1897). Archibald Geikie pointed out in 1899 that the testimony of the rocks clearly denied Kelvin's thermodynamic inference that geological activities must have been more vigorous in the past than they are today, and that the known sequence of sedimentary strata could not have accumulated within the limits set by Kelvin's solution of the problem. Moreover, James Geikie (1900) showed very convincingly that the crustal compression set up by even 100 million years of cooling would be confined to an outer shell far too thin to accommodate the immense thicknesses of folded rocks involved in the Alps and other great mountain ranges. Evidently some factor—if not more than one—had been overlooked, though few physicists were then willing to admit the possibility of any fundamental mistake. Perry, however, had already heartened the geologists by pointing out that it was allowable to assume a relatively high thermal conductivity for the deep interior of the globe, in which case the cooling of the crust would have been correspondingly slowed down. He saw no reason for denying the geologists anything up to 4,000 million years, an estimate of an order that has been confirmed by Wasiutynski in the course of a recent discussion of the earth's thermal history (1946).

Nevertheless, Kelvin's great authority compelled a compromise, and at the turn of the century geologists who claimed more than about 100 million years were thought to be unduly rash. A few, indeed, reluctantly satisfied themselves with a more meagre allowance of time, but the majority steadfastly refused to accept Kelvin's results as final. The real flaw in Kelvin's assumptions was disclosed shortly after the discovery of radioactivity, when Strutt (Lord Rayleigh) detected the presence of radium in common rocks from all parts of the world. With the demonstration that the crustal rocks contain radioactive elements and are therefore endowed with an unfailing source of heat, it became obvious that the earth is not living merely on its ancestral capital of internal heat, as Kelvin had confidently believed, but that it has an independent and regular source of income

FIGURE 1 (*above*) – *Upper Old Red Sandstone strata (age about 280 million years) resting unconformably on vertical Silurian rocks (about 320 million years) at Siccar Point, Cockburnspath, Berwickshire.*

(Photograph by H.M. Geological Survey, Crown copyright reserved)

FIGURE 2 (*below*) – *Carboniferous Limestone (about 240 million years) resting unconformably on inclined Silurian slates (about 320 million years) at Arco Wood Quarry, four miles north of Settle, Yorkshire.* *(Photograph by Professor S. H. Reynolds)*

FIGURE 3 – *Wave-swept surface of folded rocks, metamorphosed and partly granitized, representing the worn-down roots of a Pre-Cambrian orogenic belt (about 1,050–1,100 million years), at Borgå, south coast of Finland.*

(Photograph by Professor C. E. Wegmann)



FIGURE 4 – *Pleochroic halo in mica from Murray Bay, Quebec, showing well-developed rings due to α-particles shot out from a uranium-bearing crystal at the centre.*

(Photomicrograph by Professor G. H. Henderson)

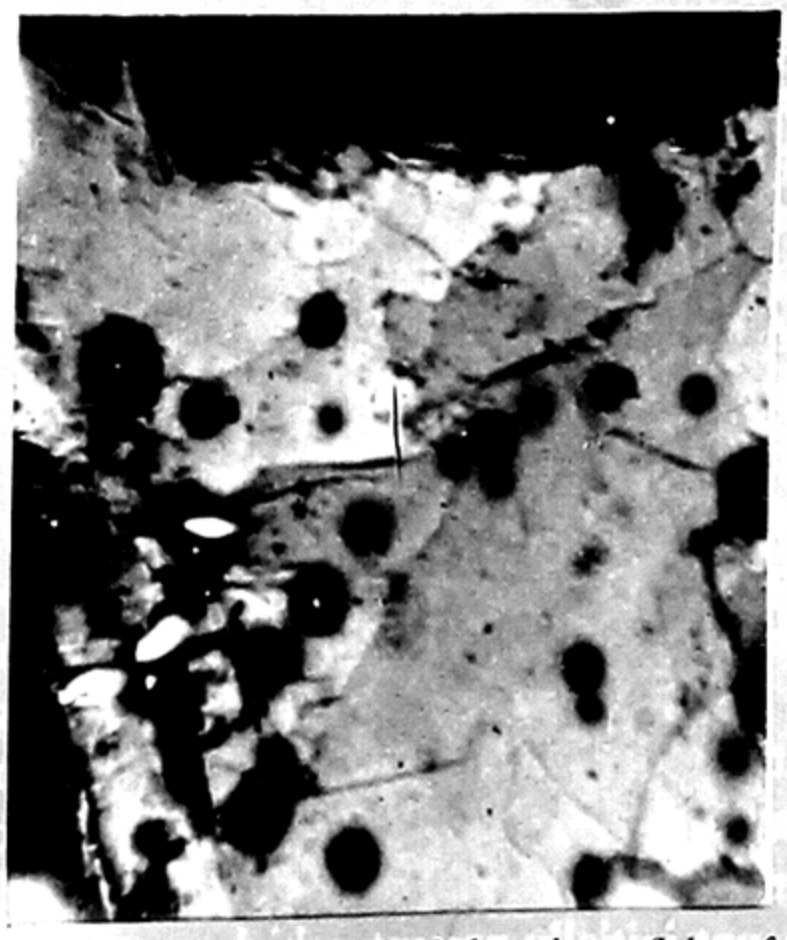


FIGURE 5 – *Pleochroic haloes in a flake of brown mica from a Pre-Cambrian granite (about 1,030 million years) from Ontario, Canada.*

(Photomicrograph by Professor G. H. Henderson)

of its own. The abundance of the radioactive elements in the crustal rocks is such that the net loss of heat is extremely low; age estimates based on the rate of cooling are therefore greatly increased. If, for example, nine-tenths of the heat-flow through the crustal rocks is of radioactive origin—and something of this order is consistent with the available evidence—then the alleged 20–40 million years of cooling has to be multiplied by 100 or more.

By this time the minds of the older geologists were no longer attuned to thinking in terms of thousands of millions of years, and few of them were prepared to take advantage of the new discoveries. This reluctance was largely due to the fact that in 1898 Joly had resuscitated Halley's suggestion for determining the age of the oceans. Adopting the simple hypothesis that—on an average—the annual amount of dissolved sodium removed by rivers from the land has remained constant throughout geological time, he found that about 80–90 million years would be required to furnish the total amount of sodium now present in the oceans. This estimate he shortly afterwards increased to 100 million years. A few years later Sollas concluded that the probable limits were 80–150 million years. In 1910 Becker, thinking it likely that the annual increments had been progressively greater in the past, reduced the probable age to about 60 or 65 million years. Indeed, Becker was sufficiently convinced of the validity of these 'short' estimates to declare that 'radioactive minerals cannot have the great ages which have been attributed to them.'

It is therefore of some importance to consider the present status of the sodium method. It appears from recent discussion of the relevant geochemical statistics (see especially Conway, 1942 and 1943) that practically all the 'chloridized' sodium in river water represents oceanic salt, either blown inland and washed down by rain, or derived from saline deposits or the pore-spaces of sediments. Allowing for such 'second-hand' salt, the present annual addition of new sodium is about 6×10^7 tons. Even this figure may be misleadingly high, because, as Lane has pointed out, analyses are rarely made of the water from rivers when they are in flood, i.e. when the content of dissolved material is at its minimum. The total accumulation of marine sodium in ocean water and sediments is estimated at about 15×10^{15} tons, less the amount initially present, which may or may not be negligible. Thus, on the assumption of past uniformity, all we can conclude is that the apparent age of the oceans is something of the order of 250 million years. But past uniformity can by no means be assumed. Present rates of weathering and erosion are far too abnormally high to be representative of the geological past. Mountain ranges and land areas in general are now much more elevated and extensive than has usually been the case. Rivers and ground waters are therefore unusually active, and, moreover, many of them drain regions that are thickly strewn with easily weathered glacial deposits. Finally, human activities of all kinds—agricultural, engineering, and chemical—have still further speeded up the rates of weathering and erosion over widespread areas.

Only a crude attempt can be made to assess the effects of these considerations on the 'apparent' age of the oceans. Figure 6 illustrates the observed fact that the continents are made up of belts of rocks that have suffered intense compression, folding, and thickening. If we imagine—going backwards in time—all the folds to be straightened out, then the crustal layer responsible for the continents becomes increasingly attenuated and extensive; so much so that in the early days of geological history this continental layer would be spread out so thin that its surface would be below sea level, and the only lands would be a few volcanic islands. Since then the continental lands exposed to erosion have, on the whole and despite wide fluctuations, progressively increased in height and area. According to this conception, the quantitative effects of denudation must have gradually increased from almost zero at the beginning to the all-time maximum of the present epoch. Roughly we may reckon that the time-average rate was probably between $\frac{1}{2}$ and $\frac{1}{3}$ of the present rate in respect (separately) of area, height, and relief. That is, it was probably between $(\frac{1}{2})^3$ and $(\frac{1}{3})^3$ of the present rate. The age of the oceans may therefore be anything between 8 and 27 times the apparent age of 250 million years, which itself may be a minimum. Obviously the hour-glass of sodium accumulation is a hopelessly variable timekeeper. The most that can be said is that its present reading is not inconsistent with an oceanic age of a few thousands of millions of years.

What we need for the accurate measurement of such immense periods is a natural process that has operated throughout geological time and has produced measurable results at a known rate, of which the law of variation with time is also known. The decay of the radioactive elements is the only known process that fulfils these stringent conditions. The radioactive methods depend on the

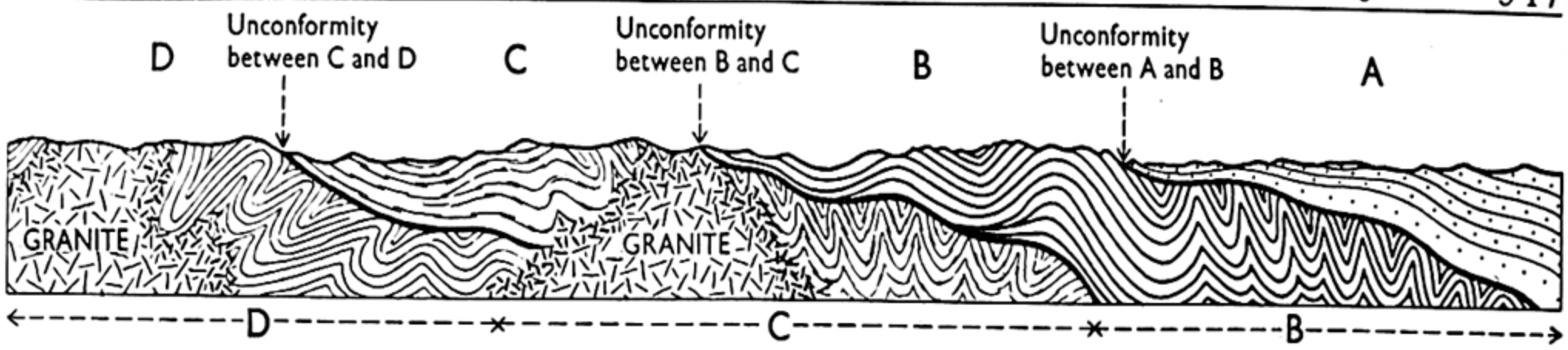


FIGURE 6 – *Diagrammatic section to illustrate the rocks and structures of a series of orogenic belts (A, B, C, and D) such as make up the continental crust of the earth. (Vertical scale greatly exaggerated.)*

transformation of uranium and thorium into helium and lead, and on the accumulation of these stable end-products in minerals and rocks that contain the parental elements. Helium, being a gas, is liable to escape, but the lead is much more likely to be retained and so to serve as an index of age. Provided a radioactive mineral such as pitchblende or uraninite has remained unaltered by weathering or other changes, then the amount of radiogenic lead now found within it is a function of (*a*) the amounts of uranium and/or thorium now present and (*b*) of the time elapsed since the mineral first crystallized. Fortunately it is possible to discriminate between the radiogenic lead and any ordinary lead that may have been present as an initial impurity in the mineral. The parental uranium contains two chemically inseparable isotopes, UI (or U^{238}) and AcU (or U^{235}), in atomic proportions having the present value AcU/UI = 1/139. Since AcU decays much more rapidly than UI, this ratio was progressively higher in the past. The material results of the atomic transformations can be summarized as follows:

$$U^{238} \rightarrow Pb^{206} + 8He$$
$$U^{235} \rightarrow Pb^{207} + 7He$$
$$Th^{232} \rightarrow Pb^{208} + 6He$$

It will be noticed that in each case a specific isotope of lead is generated. Ordinary lead is a mixture of the same three isotopes, together with a fourth, Pb^{204}, which is not known to be an end-product of radioactive decay. Thus, if the lead separated from a radioactive mineral is isotopically analysed (e.g. by means of the mass-spectrograph) and found to contain Pb^{204}, the proportion of the latter provides an index of the amount of ordinary lead that was initially present.

The present rates of production of radiogenic lead are known with a remarkable degree of accuracy, but the question naturally arises: can we be reasonably sure—apart, of course, from the inevitable slowing down due to the wearing out of the parents—that these rates have remained constant throughout geological time? In other words, can we be sure that the physical constants concerned have not varied with time? Fortunately, pleochroic haloes provide us with an unambiguous affirmative. Certain granites contain flakes of brown mica which, under the microscope, can be seen to be sprinkled with dark circular spots (figure 5, page 102). These are known as pleochroic haloes, and some of them, when highly magnified, reveal a beautifully developed pattern of concentric rings (figure 4, page 102). A minute radioactive crystal lies at the centre of each halo, and the darkening of the surrounding mica is produced by the helium atoms (α-particles) that are shot out in all directions. The radius of each ring corresponds to the range of the α-particles from one particular radioactive element. Careful measurements by G. H. Henderson (1943) show that the rings in Pre-Cambrian haloes over 1,000 million years old are just as sharply defined as those in younger rocks, and that the corresponding radii and ranges are identical. Since the range, in turn, depends on the rate of disintegration of the radioactive element concerned, it follows that the radioactive constants have not varied appreciably for at least 1,000 million years.

At any given time the rate of production of a particular lead isotope depends only on the disintegration constant and amount of the parental element then present. Thus the age of a mineral t_m can be readily calculated from each of the three ratios Pb^{206}/U, Pb^{207}/U, and Pb^{208}/Th, where these symbols here represent the percentages of the parent elements and of the isotopes of radiogenic lead now present in the mineral under investigation. The respective equations for t_m are (Keevil, 1939):

$$t_m = 15{\cdot}15 \times 10^9 \log_{10} (1 + 1{\cdot}158\ Pb^{206}/U) \text{ years}$$
$$t_m = 2{\cdot}37 \times 10^9 \log_{10} (1 + 159{\cdot}6\ Pb^{207}/U) \text{ years}$$
$$t_m = 46{\cdot}20 \times 10^9 \log_{10} (1 + 1{\cdot}116\ Pb^{208}/Th) \text{ years}$$

A fourth value for t_m can be found from the ratio Pb^{207}/Pb^{206}.

If a mineral has remained unaltered, then all

four values for t_m should be in close agreement. In practice this rarely happens, because, even in the freshest-looking mineral, migrations of the critical elements are likely to have occurred. Fortunately, even if the three values for t_m based on Pb^{206}/U, Pb^{207}/U, and Pb^{208}/Th are widely different the relations between them provide criteria for assessing the true age (figure 7). If there has been leakage of radon (the gaseous member of the U1 family), then the mineral is necessarily deficient in Pb^{206}; in this case the most probable age is given by Pb^{207}/U (see Wickman, 1942, and Holmes [5], 1947*b*). If there has been loss of Pb or U or both, or gain of either or both, then the true age, or a close approximation to it, is given by Pb^{207}/Pb^{206}.

Although a great many radioactive minerals have been chemically analysed, relatively few isotopic analyses of the lead have been made as yet. Professor A. O. Nier, following up Aston's pioneer work, has been the most active and successful worker in this field. As an example of a fully investigated mineral, samarskite from Spinelli Quarry, Portland, Connecticut, may be taken. The mineral occurs in a pegmatite dating from about the end of the Devonian period.

	Pb	*U*	*Th*	*'Apparent Age' from total Pb (million years)*
Percentages (R. C. Wells)	0·314	6·91	3·05	295

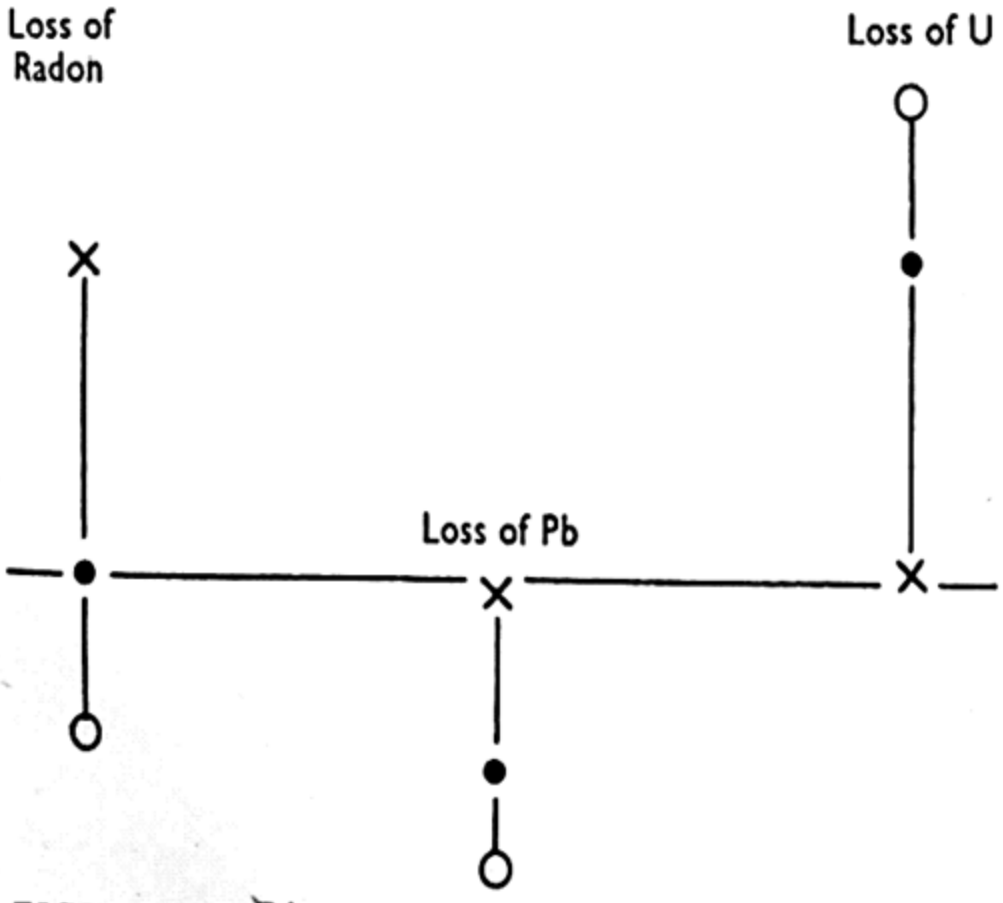


FIGURE 7 – *Diagram to illustrate the effects of various types of alteration on the apparent ages of a radioactive mineral calculated from Pb^{206}/U (open circles); Pb^{207}/U (solid circles); and Pb^{207}/Pb^{206} (crosses). The horizontal line represents the true age of the mineral, points above and below being respectively too high and too low.*

Isotopic Proportions (Nier *et aliter*)	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
In total lead ..	0·167	100·00	7·60	21·30
In original lead	0·167	3·04	2·61	6·35
In radiogenic lead	—	96·96	4·99	14·95
Percentages ..	—	0·236	0·012	0·036
Age Ratios	$\frac{Pb^{207}}{Pb^{206}}$	$\frac{Pb^{206}}{U}$	$\frac{Pb^{207}}{U}$	$\frac{Pb^{208}}{Th}$
	0·0515	0·03415	0·00174	0·0118
Values of t_m (million years)	256	255	254	266

Here the agreement is unusually good, and it can be concluded that about 255 million years have elapsed since the close of the Devonian period.

In the following table some of the better-established dates are listed:

Mineral	*Locality*	*Geological Age*	*Probable Age (millions of years)*
Pitchblende	Colorado	Beginning of Tertiary	58
Pitchblende	Bohemia	Late Carboniferous	215
Samarskite	Connecticut	End of Devonian	255
Cyrtolite	New York	End of Ordovician	350
Kolm	Sweden	Upper Cambrian	440
Pitchblende	Katanga, Belgian Congo	Pre-Cambrian	580
Uraninite	Morogoro, Tanganyika	Pre-Cambrian	590
Uraninite	Besner, Ontario	Pre-Cambrian	760
Bröggerite	Moss, S. Norway	Pre-Cambrian	860
Uraninite	Wilberforce, Ontario	Pre-Cambrian	1,035
Cleveite	Aust Agder, S. Norway	Pre-Cambrian	1,075
Pitchblende	Great Bear Lake, Canada	Pre-Cambrian	1,330
Uraninite	N.E. Karelia, U.S.S.R.	Pre-Cambrian	1,765
Uraninite	Huron Claim, Manitoba	Pre-Cambrian	1,985

The uraninite from Manitoba is the oldest mineral so far investigated, and its great age is roughly confirmed by analyses of another uraninite and of two monazites, all from the same pegmatite. The 'apparent ages' of these, calculated from the total lead, are 1,950, 1,955, and 1,990 million years respectively. The pegmatite represents the closing phase of the plutonic activity of a typically Archaean orogenic belt. It followed a long series of granitic and other plutonic rocks, which in turn are emplaced within a thick sequence of metamorphosed volcanic and sedimentary rocks. The

latter include still recognizable conglomerates, containing pebbles of pre-existing granites and quartzites, which must therefore be well over 2,000 million years old. Since the earth must be older still, this figure can be regarded as a conservative minimum for its age.

To find a maximum for the age of the earth we may assume that when the earth began it was free from the lead isotope Pb^{207}, and that all the Pb^{207} now present in the common granitic rocks of the continental crust has since been generated from U^{235}. Granitic rocks contain on an average about 20 parts per million of lead and 3·5 parts per million of U. The isotopic constitution of granitic lead has not yet been determined directly, but isotopic analyses of several samples of lead from galena and other lead ores of Tertiary age have been made by Nier and his co-workers. These ores represent concentrations of the granitic lead of some 25 million years ago, which is near enough to the present for our purpose. The average isotopic abundances of Tertiary lead are:

Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}	*Total (parts per million)*
1	18·54	15·55	38·28	73·37

corresponding in parts per million very nearly to

0·27	5·1	4·2	10·4	20

in the average granitic rocks of today. Inserting the value $Pb^{207}/U = 4{\cdot}2/3{\cdot}5$ in the appropriate formula given on page 104, the time required for the generation of all the Pb^{207} is found to be 5,400 million years. The age of the earth is therefore somewhere between 2,000 and 5,400 million years.

Can we arrive at a closer estimate? I think we can, again by making use of the invaluable data provided by Nier (see Holmes, 1946). Nier and his co-workers have determined the relative abundances of the isotopes in twenty-five samples of lead from common lead minerals of various geological ages. The results, graphically summarized in figure 8, reveal internal relationships between Pb^{206}, Pb^{207}, and Pb^{208} that are almost exactly what they would be if the primeval lead originally present in the material of the outer earth had been slowly modified by additions of radiogenic lead. A few of the samples have a more or less abnormal constitution, but, apart from these, the evidence is clear that ore-lead represents a concentration of the lead that was dispersed through the crustal rocks of the region concerned at the time when the ore deposition took place.

The problem, then, is this: knowing the isotopic constitution of rock-lead as it was at various periods ranging from 1,330 million years ago (the Great Bear Lake sample) to 25 million years ago (the Tertiary samples), to find the relative abundances of Pb^{206} and Pb^{207} in the earth's primeval lead and the time that has elapsed since that primeval lead began to be modified by radiogenic additions. This time (t_o) is the required age of the earth.

Using the following symbols, with t_m for the age of the lead ore:

	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
Ore-lead (≡ rock-lead) ..	1	a	b	c
Primeval lead	1	x	y	z
Radiogenic lead (from t_o to t_m)	—	$a-x$	$b-y$	$c-z$

we can write:

$$\frac{b-y}{a-x} = r = \frac{\text{No. of atoms of } Pb^{207} \text{ generated from } t_o \text{ to } t_m}{\text{No. of atoms of } Pb^{206} \text{ generated from } t_o \text{ to } t_m}$$

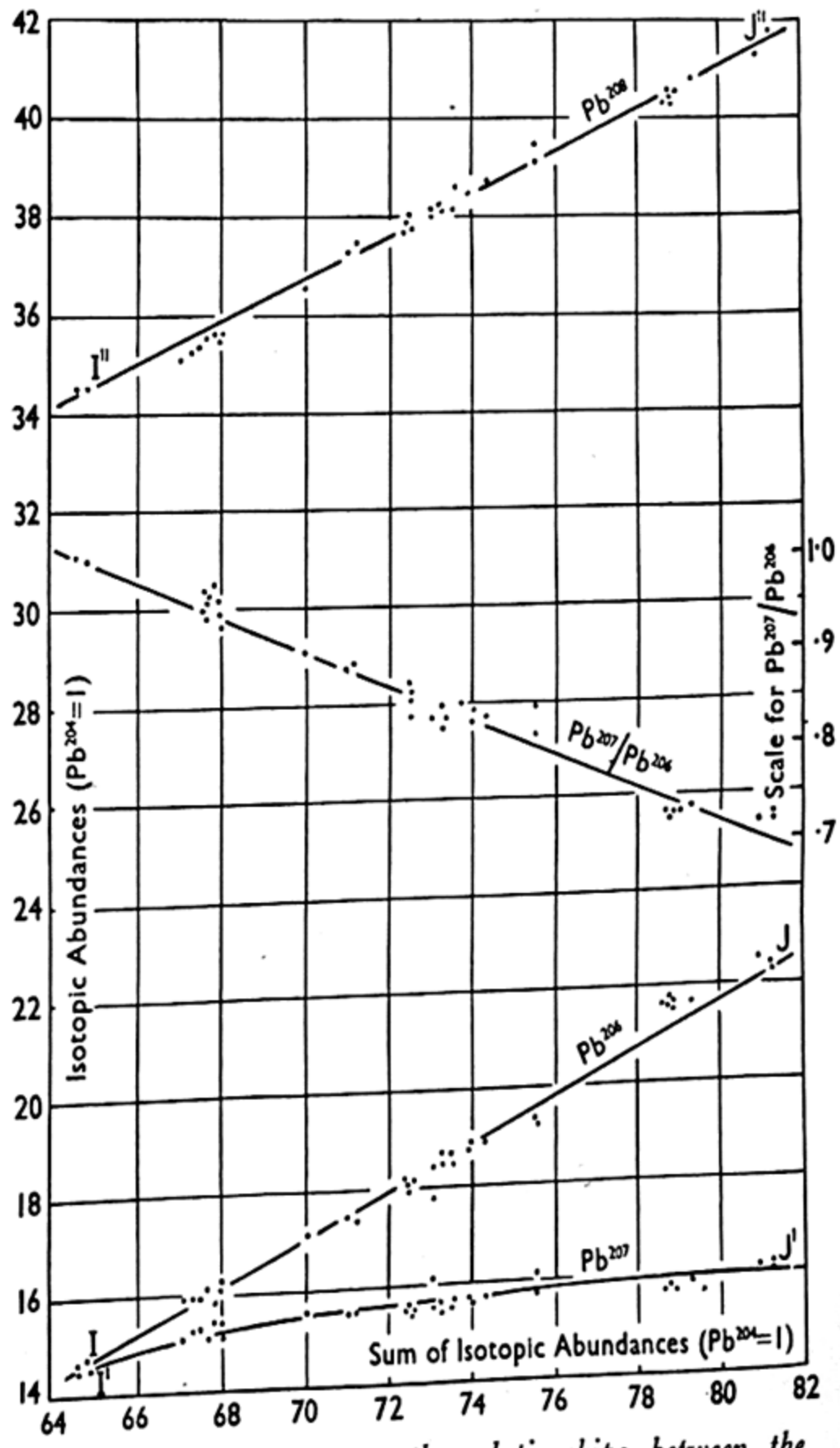


FIGURE 8 – *To illustrate the relationships between the abundances of Pb^{206}, Pb^{207}, and Pb^{208} (relative to Pb^{204} = 1) in lead samples prepared from common ores of lead.*

From the expression on the right r can be calculated (for each appropriate value of t_m) for various assigned values of t_o from 2,000 to 5,000 million years. For each assigned value of t_o we have:

$$ar - xr = b - y \quad \text{for a lead sample of age } t_m$$

and $$a'r' - xr' = b' - y \quad \text{for a lead sample of age } t_m'$$

whence $$x = \frac{b - b' + a'r' - ar}{r' - r}$$

and $$y = b + rx - ar$$

Taking samples 25 and 18 (figure 10, page 108), the following results are obtained:

No. 25 Galena, Great Bear Lake (Pre-Cambrian)	*No. 18 Galena, N. Carolina (Late Carboniferous)*
$a = 15{\cdot}93$	$a' = 18{\cdot}43$
$b = 15{\cdot}30$	$b' = 15{\cdot}61$
$t_m = 1{,}330$ million years	$t_m' = 220$ million years

When $t = 2{,}500$ million years:

$r = 0{\cdot}23305$ $\quad r' = 0{\cdot}16999$

$x = 14{\cdot}11$ $\quad y = 14{\cdot}87$

When $t = 3{,}000$ million years:

$r = 0{\cdot}30156$ $\quad r' = 0{\cdot}22794$

$x = 12{\cdot}40$ $\quad y = 14{\cdot}24$

When $t = 3{,}500$ million years:

$r = 0{\cdot}39685$ $\quad r' = 0{\cdot}30985$

$x = 10{\cdot}59$ $\quad y = 13{\cdot}18$

Plotting x against t, a curve AB is drawn; a point representing a solution for x and t_o lies somewhere on this curve or its continuation. Dealing in the same way with another pair of lead samples, such as No. 1 (galena, Peru, Tertiary, 25 million years) and No. 19 (galena, Ivigtut, Greenland, Late Pre-Cambrian, 600 million years), a curve CD is similarly constructed. Where the two curves intersect (at P in figure 10) $x = 1{\cdot}22$ and $t_o = 3{,}330$ million years.

In the same way we can plot y against t and construct two curves that intersect at $y = 13{\cdot}71$ and

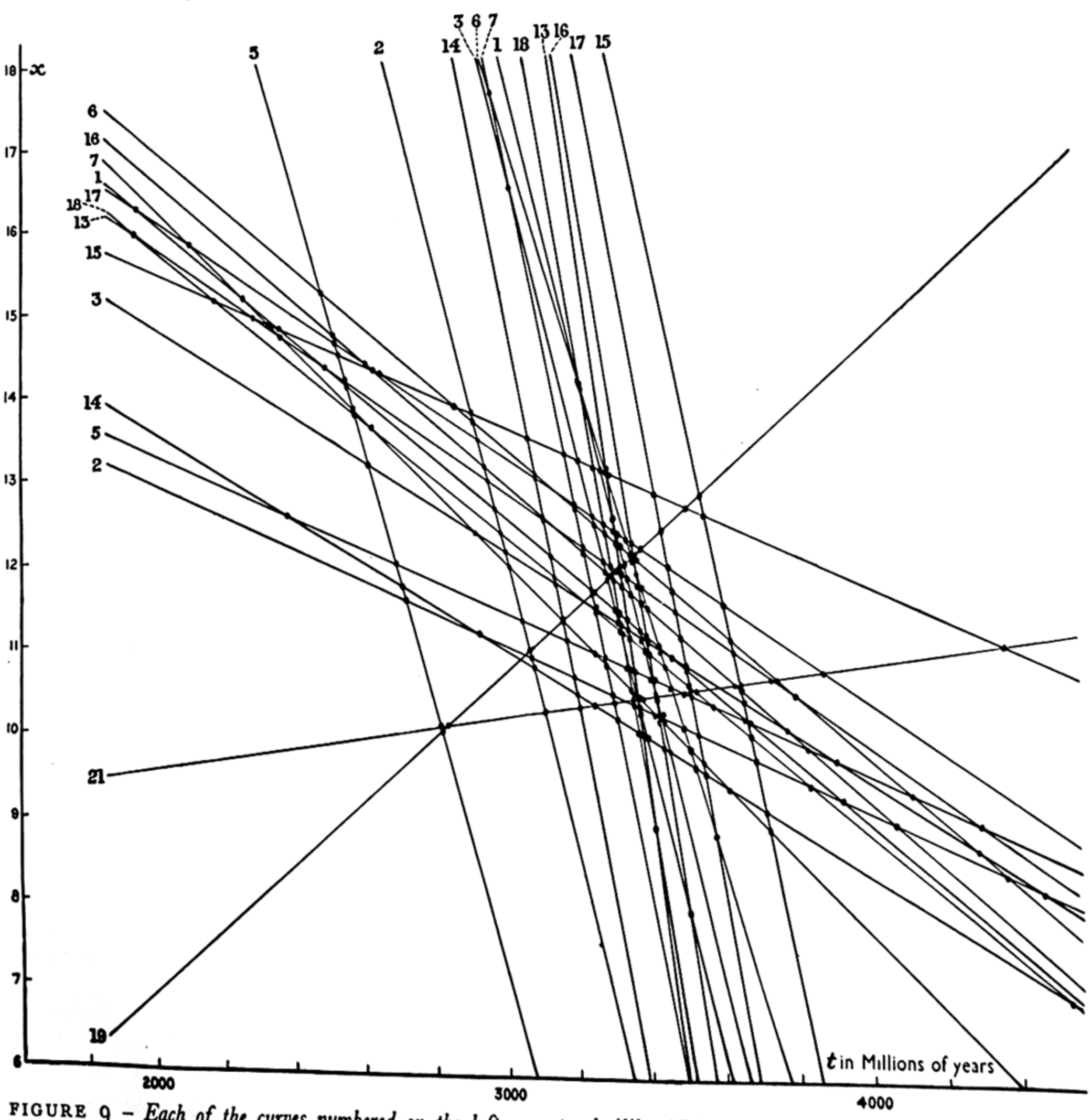


FIGURE 9 – *Each of the curves numbered on the left corresponds (like AB in Figure 9) to a pair of lead samples, of which No. 25 is one. The curves similarly based on No. 19 are numbered along the top. The numbers are those of Nier's lead samples as listed in Holmes (1946). Each intersection, marked by a dot, provides a solution for x and t_o.* (*See page 108.*)

t_o = 3,330 million years. The two pairs of curves, based on the data for two pairs of lead samples, thus yield a solution of the problem.

Obviously a great many solutions can be obtained by this method. Figure 9 illustrates the *xt* curves for pairs made up of No. 25 with each in turn of fourteen younger lead samples, and for pairs made up of No. 19 with 11 younger lead samples. The intersections provide over two hundred solutions, with a marked concentration at about 3,300–3,400 million years.

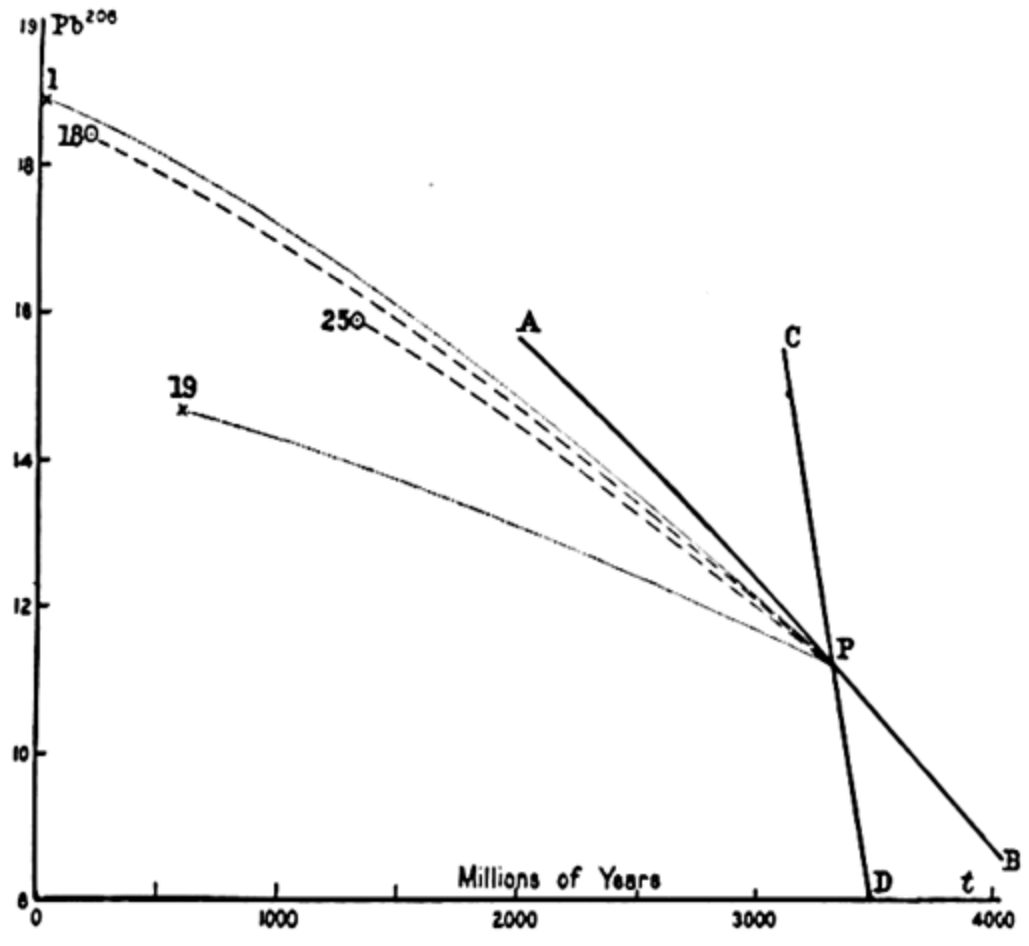


FIGURE 10 – *The curve AB indicates the variation of x (primeval Pb^{206}) with assigned values of t for the pair of lead samples 25 and 18. CD represents the corresponding variation for the pair 19 and 1. The intersection at P gives a solution for x and t_o. The lines joining P to the points representing the lead samples (a and t_m in each case) show the gradual increase of Pb^{206}, relative to Pb^{204} = 1, from x to a during the period t_o–t_m.* (*See page* 107.)

obtained for t_o, *x*, and *y*. The average value of t_o is 3,290 million years, but a histogram of the t_o values (figure 11) reveals a well-marked mode at 3,350 million years, which is found to be somewhat better than the average value when tested by a least-squares method (Holmes [5], 1947*a*). The dotted frequencies on the left of figure 11 illustrate the lopsided effect of including results involving the data for two lead samples of

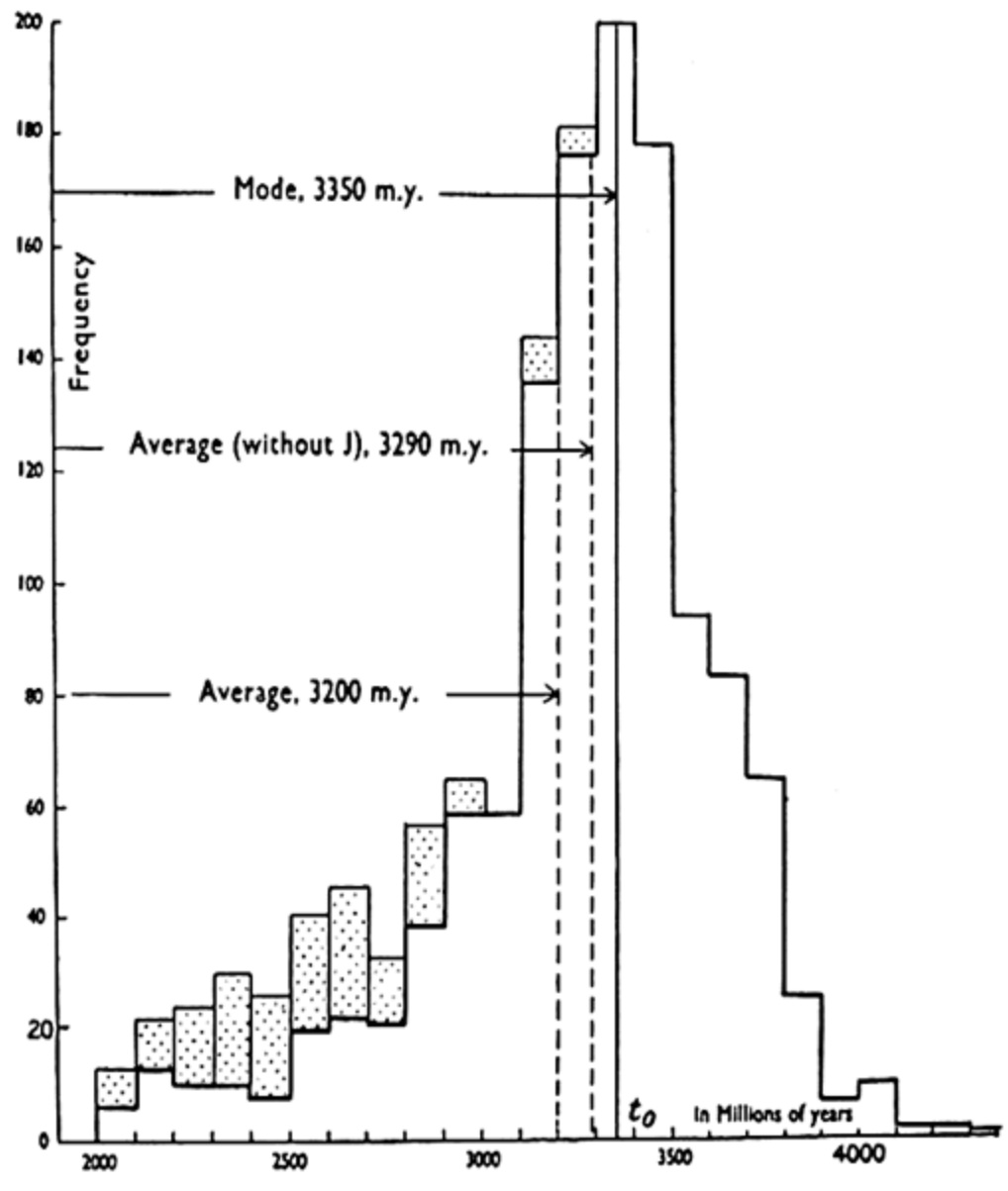


FIGURE 11 – *Histogram representing the frequency distribution of 1,419 solutions for t_o to within ranges of 100 million years. The frequencies of 162 solutions involving the abnormal Joplin lead samples (Nos. 9 and 11) are indicated by the dotted areas. The histogram for the 1,257 solutions without the aberrant Joplin results is outlined boldly.*

Additional sets of curves can be constructed for pairs based on No. 23 (cerussite, Broken Hill, N.S.W., 1,200 million years); No. 22 (galena, same locality and age); and No. 21 (galena, Quebec, 800 million years). From the intersections of all five sets of curves, and those of the corresponding *yt* curves, 1,257 solutions have been abnormal constitution. Certain other abnormal leads, however, would give a concentration of results on the right. The fact that the modal solution remains independent of these aberrant results favours the hope that an estimate of 3,350 million years for the age of the earth is unlikely to be seriously wrong.

REFERENCES

[1] Conway, E. J. *Proc. Roy. Irish Acad.*, 1942, **48, B8**, 119–59; 1943, **48, B9**, 161–212.
[2] Henderson, G. H., and Bateson, S. *Proc. Roy. Soc.*, 1934, **145A**, 563–81.
[3] Henderson, G. H., and Turnbull, L. G. *Ibid.*, 1934, **145A**, 382–91.
[4] Holmes, A. *Nature*, 1946, **157**, 680–4; *ibid.*, 1947*a*, **159**, 127–8.
[5] *Idem. Trans. Geol. Soc. Glasgow*, 1947*b*, **21**, 117–52.
[6] *Idem. Geol. Mag.*, 1947*c*, **134**, 123–6.
[7] Keevil, N. B. *Am. Journ. Sci.*, 1939, **237**, 195–214.
[8] Nier, A. O. *Journ. Am. Chem. Soc.*, 1938, **60**, 1571–6.
[9] *Idem. Phys. Rev.*, 1939, **55**, 153–63.
[10] Nier, A. O., Thompson, R. W., and Murphey, B. F. *Phys. Rev.*, 1941, **60**, 112–16.
[11] Wasiutynski, J. *Astrophys. Norvegica*, 1946, **4**, 225.
[12] Wickman, F. E. *Geol. Fören. Förh.*, 1942, **64**, 465–76.
[13] *Idem. Sveriges Geol. Undersökning*, 1939, **C, 427**, 1–8; 1944, **C, 458**, 1–6.

James Hutton, the founder of modern geology: 1726–97

M. MacGREGOR

The second half of the eighteenth century was a period of intense intellectual activity in Scotland. Among the greatest of the many distinguished figures of the time was James Hutton, whose geological researches and writings established the fundamental principles of modern geology. He was the first to recognize and describe the processes which determine the past and present configuration of the earth, drawing his evidence not from the academic speculations in which his contemporaries indulged but from the rocks themselves.

The 26th of March, 1947, saw the hundred and fiftieth anniversary of the death of James Hutton, who has been so often acclaimed as the founder of modern geology. The memory of this great Scotsman is still green, not only in the little northern kingdom where he was born and where he laboured, but throughout the scientific world. To the generality of people he is perhaps best known as the author of the often-quoted saying that in the operations of nature 'we find no vestige of a beginning—no prospect of an end,' words that were startling and indeed iconoclastic when they were written in 1785. At this distance of time it is difficult for us to measure the debt we owe to Hutton's genius or to realize how profoundly the principles he established came to revolutionize the whole trend of scientific speculation. To appreciate the fundamental importance of his work and its far-reaching repercussions, it must be set against the background of the time in which he wrote; and to return to the latter half of the eighteenth century is to enter a new and strange geological world, differing from our own in its concepts and scope. It was a world given over to dogmatisms and preconceived theories, to fantastic explanations invoked to account for natural phenomena, to barren speculations that sought to bring the facts of nature into conformity with the traditional Mosaic chronology. A universal ocean in which the solid rocks now forming most of the dry land had been deposited as chemical precipitates, a succession of sudden, catastrophic events such as the violent, tumultuous upheaval of mountain ranges, and above all, the limitation of the time available for geological changes to a few thousand years, were amongst the commonly accepted tenets of the time. Under these conditions progress in geological research was narrowed and obstructed, and it was Hutton who, by uprooting and sweeping away all such sterile conceptions, placed geology on a solid and secure foundation. To free geology of its accumulated traditions, false analogies, and misconceptions was a Herculean task, but it was a task which he carried out quietly and courageously. To study and understand the processes at work on the surface of the earth, to frame a system of philosophy which would explain them, and to show from the records of the solid rocks themselves that the same processes have operated throughout immeasurable time—this was the work to which he devoted long years of patient observation and reflection. His *Theory of the Earth* is unquestionably one of the great classics of science, by virtue of its wide sweep, its originality, and its irresistible logic. There were no assumptions, no unverified propositions in his doctrine, no principles allowed that were not first submitted to the test of observation. He uses the word 'observable'



Reproduction of medallion portrait of James Hutton, M.D.

in the sub-title of his famous memoir of 1785, describing it as 'An Investigation of the Laws observable in the Composition, Dissolution, and Restoration, of Land upon the Globe.' Nature herself was to him the ultimate court of appeal. In one memorable passage he wrote: 'It is only in knowing the succession of things, that natural appearances can be explained; and it is only from the examination of those appearances, that any certain knowledge of this operation is to be obtained. But how shall we acquire the knowledge of a system calculated for millions, not of years only, nor of the ages of man, but of the races of men and the successions of empires? There is no question here with regard to the memory of man, or any human record, which continues the memory of man from age to age; we must read the transactions of time past, in the present state of natural bodies; and, for the reading of this character, we have nothing but the laws of nature, established in the science of man by his inductive reasoning.'

HUTTON'S LIFE AND TIMES

Hutton's life-story can be simply told. He was born at Edinburgh on 3rd June, 1726, the son of a merchant who had for a time held the office of City Treasurer. He studied medicine for three years at Edinburgh University and for two years in Paris before taking his doctor's degree at Leyden in 1749. On his return home he decided to abandon medicine for farming, and with this end in view spent two years (1752–4) in Norfolk learning agricultural methods. These years in Norfolk were important and formative ones, because it was at this period that his early passion for scientific research turned definitely in the direction of geology. In 1754 he settled down in Berwickshire, where he devoted himself to the cultivation and improvement of the little estate which had been bequeathed to him by his father. He continued his geological investigations, however, making many excursions to different parts of the country and amassing a wealth of observations and records which he was later to put to such splendid use. About the year 1768 he determined to let his estate and to retire to Edinburgh, and it was in Edinburgh that the last twenty-nine years of his life were passed. It was retirement but in no sense leisure, for Hutton was a man of unwearied industry. He had many interests—philosophy, chemistry (he was partner in a firm manufacturing ammonium chloride), meteorology, and agriculture. He published volumes on physics and metaphysics, including a three-volume treatise entitled *An Investigation of the Principles of Knowledge, and of the Progress of Reason from Sense to Science and Philosophy*. He made a number of important meteorological studies, and he left behind him in manuscript a lengthy treatise on agriculture (now in the possession of the Geological Society of Edinburgh). But his main passion and his main life-work lay in the study of the rocks, minerals, and soils of his native land.

In Edinburgh he had a number of intimate and scholarly friends who took a keen interest in his work, and with whom he could discuss the new ideas which filled his mind: Joseph Black (1726–99), the distinguished chemist, who has sometimes been termed the father of modern chemistry just as Hutton himself has been called the father of modern geology; John Clerk of Eldon, 'that country gentleman who, with pieces of cork on his own dining table, invented modern naval warfare'; John Playfair (1748–1819), who was in later years to write a biographical account of his friend and to produce that inspiring and lucid masterpiece *Illustrations of the Huttonian Theory of the Earth* (1802); and Sir James Hall of Dunglass (1762–1831), who has recorded that 'after three years of almost daily warfare with Dr Hutton on the subject of his theory, I began to view his fundamental principles with less and less repugnance,' and who was later to bring powerful experimental support to Hutton's view that crystalline rocks could under certain conditions be produced by the cooling of originally molten material. It was in 1785, some seventeen years after his return to Edinburgh, that Hutton read before the Royal Society of that city his memoir or essay entitled *Theory of the Earth*. This memoir, occupying ninety-six quarto pages, was published in the first volume of the Society's *Transactions*.[1] A violent and unworthy attack on his *Theory* by a Dublin mineralogist in 1793, an attack which not only travestied Hutton's views but accused him of atheism, made him decide to extend and revise his 1785 memoir and to prepare and publish a more elaborate and complete statement of his position. In this task, weakened by illness as he was (he was now 67 years old), he persevered resolutely, and the immortal *Theory of the Earth, with Proofs and Illustrations* appeared in two octavo volumes in 1795. A third and concluding volume was left in manuscript at Hutton's death in 1797. The only four chapters of this volume that are

[1] See 'The Royal Society of Edinburgh,' by Professor J. Kendall (ENDEAVOUR, V, 18, April 1946).

known to have been preserved were published in 1899 by the Geological Society of London.

THE HUTTONIAN THEORY

Hutton's *Theory of the Earth* was wide-ranging in its scope, and the many unique contributions it made to geological research are without parallel in the history of the science. It was little noticed during his lifetime, and, indeed, the long controversy between the Neptunists, as those who adhered to the doctrine of a universal and gradually subsiding ocean were called, and the Plutonists, as the followers of Hutton were termed, did not die away until the first quarter of the nineteenth century had gone. It may be useful to give here one illustration of the divergence of views between the two schools. Granite, according to the Neptunists, was a rock of aqueous origin, the first to be laid down as a precipitate from the hypothetical universal ocean. Hutton, on the other hand, taught that granite had once been molten and had been intruded among the rocks in which it is found; and he pointed triumphantly to the observations he had made in Glen Tilt to show that granite veins emanating from the parent body entered and penetrated the surrounding rocks. He was beyond doubt the founder of physical and dynamical geology. He was one of the earliest geologists to stress the denuding and erosive power of running water and the part it played in the formation of valleys; he was the first geologist to recognize that denudation and deposition were closely linked aspects of the same natural process; and he was the first to see clearly that a succession of slow and slight effects would lead inevitably, if given a sufficient length of time, to widespread physiographic changes. It was consummate genius that led him to take the next step in the development of his argument. He turned to the solid rocks to find in them evidence that the same processes of change as he saw in the world around him must have operated again and again in the remote past. As he himself phrased it: 'the present is the key to the past.' The scenery of today is but the latest phase in a long-continued and ever-changing succession of landscape panoramas. One land mass is worn down and the waste products provide the materials for a new one, and continent follows continent in the eternal revolution of nature. Such, in outline, was Hutton's theory, and to the process as he envisaged it he could see neither beginning nor end.

He was the first geologist to recognize the importance of unconformities as providing clear proofs of the cycle of destruction and reconstruction, citing the now classic examples in North Arran, in the Jed near Jedburgh, and at Siccar Point on the Berwickshire coast. He realized that there must exist in nature some powerful force or agency which could elevate the solid rocks formed on the sea floor into new lands, and so initiate a fresh cycle of erosion. This force he found in subterranean pressures, due essentially, he believed, to the effect of heat transmitted from the interior of the earth. It was only by the action of powerful upward pressures that, to quote his own words, 'every species of fracture, dislocation, and contortion . . . and every degree of departure from a horizontal to a vertical position' seen in the uplifted strata could be explained. When he speaks of rock masses as having 'undergone a double course of mineral changes and displacement,' adding that 'consequently the effect of subterranean heat or fusion must be more apparent, and the marks of their original formation more and more obliterated,' geologists will recognize the germ of the hypothesis of regional metamorphism.

In the sphere of igneous geology Hutton's researches were of profound significance. He was the first geologist to assert and to demonstrate the essential differences between molten material poured out at the surface (lavas) and molten material solidified at depth and under great pressures. He was the first to recognize the intrusive character of the granites, whinstones, and porphyries which he encountered in his travels, and of the dykes and veins emanating from the deeper-seated eruptive masses. He noted also the disturbances and the displacements they caused during their intrusion, and the metamorphic effects (to use a modern phrase) they produced upon the strata they cut.

As has been already said, Hutton's *Theory* received little attention during his lifetime. But there was no gainsaying its originality, its magnitude, and its grandeur of conception. It contains the first statement of many of the most fundamental principles of modern geology. 'The very obviousness and familiarity of his doctrine at the present time,' wrote Sir Archibald Geikie, 'when it has become the groundwork of modern geology, are apt to blind us to the genius of the man who first conceived it, and worked it into a harmonious and luminous whole.' Other workers had gone some way along the path that Hutton travelled; he alone reached the mountain tops from which he could see, as it were, the past history of the world unroll itself before him.

The chemistry of glass coloration

L. M. ANGUS-BUTTERWORTH

The making and working of coloured glasses are among the world's most ancient crafts. Although the empirical methods of the early workers produced results of great beauty, the study of the chemical processes involved has proved a fruitful field of research. The present extensive use of coloured glasses in scientific apparatus, signalling lamps, photographic filters, and other equipment demands a standardized product which is obtainable only as a result of knowledge of the chemical reactions involved and careful control of manufacturing processes.

INTRODUCTION

The history of coloured glasses is longer than that of the transparent white variety. For many centuries before clear glass appeared a large number of different coloured forms had been in common use.

Some of the glazed tiles covering the walls of early Egyptian chambers were magnificent examples of colouring, and polychromes as well as single colours were achieved. Pieces have been found of a vase, bearing the name of a king living in 5000 B.C., which was glazed in green inlaid with purple. Some of the most important colouring oxides employed in glassmaking today, including those of copper, manganese, and cobalt, were known to the Egyptians. Transparent glass did not appear in Egypt before about 660 B.C., when bottles and a few other objects were made of it.

From these early beginnings in Egypt the art of coloured glassmaking gradually spread. One of the first uses of coloured glass in England was in cathedral windows.

A common belief is that we do not know today how to reproduce the brilliant colours of the early cathedral windows. This was partly true up to about a hundred years ago, but today the glass technologist certainly knows far more about colours in glass than was ever known before.

A further point in connection with old cathedral glass is that when originally placed in position it was often very crude in colour and dark in shade. It has taken hundreds of years to become mellowed. Atmospheric attack on the outside of church windows has been the chief agent in creating the beautiful effects we know today. Throughout the centuries there has been steady abrasive action through the rain being driven against the glass by the wind, and chemical dissolving action through the slight acid content of much of our rain water, especially in towns. The combination of these two forces has gradually changed thick and comparatively dark glass to glass which in some cases is as thin as tissue paper and which now has light and vivid colours.

Even the impurities in the metals, which the early glassmakers could not control, gave variety to their products. It was of little consequence if the glass they supplied for church windows never had quite the same colour twice. Exciting surprises were possible—not as in the dull modern world, in which glassmaking materials and processes are so carefully and completely controlled that results are (or should be) well ascertained in advance.

It is convenient to consider the agents for the production of each of the common colours in glass in turn.

BLACK

Cobalt and nickel oxides are used together to give opaque black glasses. Nickel glasses are noted by Professor Woldemar Weyl as absorbing nearly the entire visible spectrum with the exception of the extreme red.

A small antique glass bowl of an almost jet-black colour shown to the author on one occasion by the late Sir William Boyd Dawkins had certainly a high concentration of manganese as the principal colouring agent, possibly with the addition of a little cobalt.

BLUE

Cobalt and copper serve as the usual agents for colouring glasses blue. Of the two, cobalt is the more commonly used. It transmits a deep red band in addition to blue. Accordingly, if a cobalt blue is combined with a copper bluish green, the latter absorbs the red and an excellent blue glass is obtained. If, however, the colour required is to be midway between blue and green, as in signal lenses, copper is used in association with a small amount of iron.

Weyl observes that from the viewpoint of glass technology we need only consider cobalt compounds which are derived from the bivalent cobalt ion, as tervalent cobalt is not stable in the







FIGURE 1 (*above*) – *'The Annunciation,' from St Ouen, Rouen. Fourteenth century. An example of rich colouring in glass. The prominent yellow is from oxide or chloride of silver.*

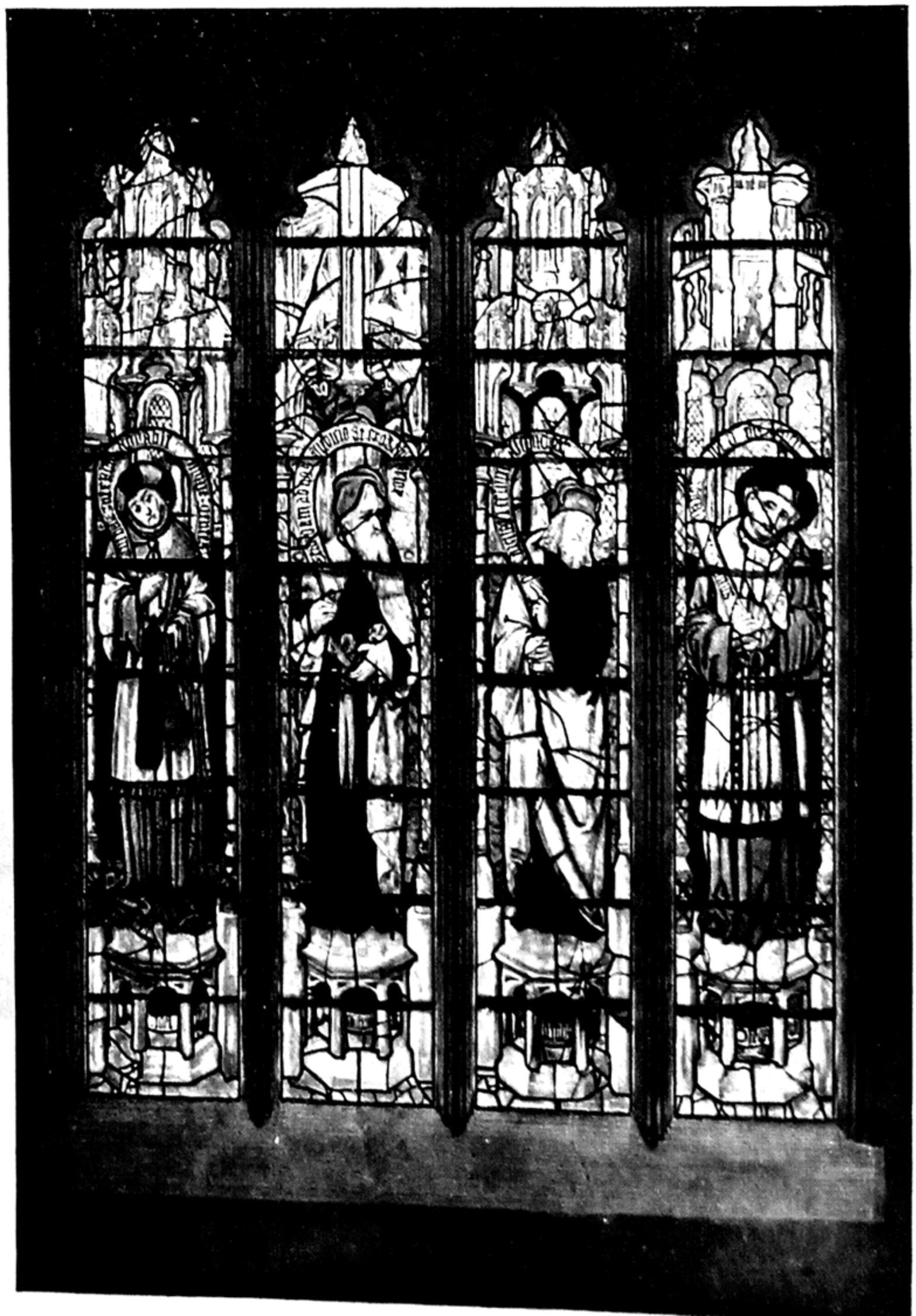


FIGURE 2 (*right*) – *Figures of the prophets from the north aisle of the nave, Fairford. Late fifteenth century. The more subdued colouring of a late period window. The red is probably a flashed gold ruby.*



FIGURE 3 (*above*) – *Part of Crucifixion window, Poitiers. Late twelfth century. A brilliant polychrome in glass, showing the command which the glassmaker possessed over his materials even at this early date. Copper and manganese are among the colouring agents used.*

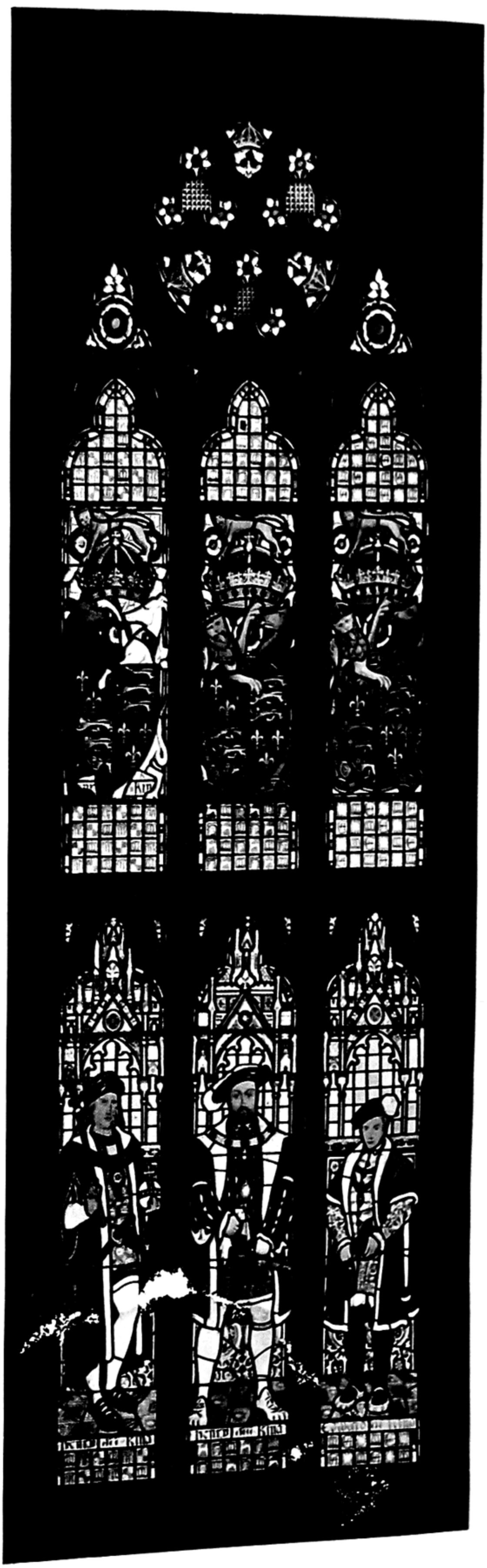


FIGURE 4 (*right*) – *A fine modern example of the use of stained glass for the decoration of a secular building. The red of the Tudor dragons is derived from selenium. The olive-green cloak of Edward VI (right) is from oxide of iron. From the Town Hall, Rochdale.*





FIGURE 5 (*above*) – *St Luke, from choir clerestory of St Ouen, Rouen. Fourteenth century. The rich ruby red of the mantle is probably from gold chloride. The object of the light grisaille staining is to allow more illumination than is obtainable through the richer but deeper colour of the central figure.*

FIGURE 6 (*left*) – *Colours in glass enable the pomp and circumstance of heraldry to be displayed to special advantage. The colour of the royal robes of Richard II (centre) is from cobalt oxide. From the Town Hall, Rochdale.*



FIGURE 7 (*left*) – *Bristol decanter. About* 1770–80. *An early form of wine decanter. The vivid blue is derived from copper.*

FIGURE 8 (*below, left*) – *Primitive glass vase, probably from Greek islands. In the attractive decoration of this vase the yellow colour is probably derived from antimony and the blue from copper.*

FIGURE 9 (*below, right*) – *Saracenic enamelled glass. Thirteenth century. This elegant vase is decorated with a blue which is a soda-copper silicate, and an opaque red from oxide of iron, the whole enriched with gold brocading to accentuate the design.*







temperature range required for glass melting. It has been found that potash glasses give a purer blue than the corresponding sodium glasses, and that borosilicates yield a reddish hue.

An interesting modern use of cobalt is in connection with glassware for lighting. If small amounts of cobalt, manganese, and copper oxides are used together in the batch, what is now known as the daylight effect is obtained. What happens is that these oxides eliminate part of the light from the artificial light sources, and the filtered remainder more closely resembles natural sunlight.

Sir Herbert Jackson suggested that the production and properties of glasses containing copper are representative of those in which the colouring is diffused in very minute particles throughout the glass, and which can be compared with colloidal solutions. In contrast to this, cobalt glasses are examples of those in which the colouring agents are in a state resembling solution, which might be compared to aqueous solutions of coloured salts.

Gmelin noted in 1779 that glasses containing iron became blue when founded under strongly reducing conditions, but no explanation was then possible. The colour was later attributed to a modification of ferric oxide which is stable only in the presence of ferrous oxide. This involves the existence of the two states of valency in the glass, or the simultaneous presence of FeO and Fe_2O_3. The addition of limestone to the melting glass may cause the colour to change to blue, as it may contain some material which acts as a reducing agent.

GREEN

For the production of green glasses iron, copper, and chromium are employed. Other possible agents, such as stannic oxide, are very rarely used.

The presence of 0·23 per cent. Fe_2O_3 gives an almost colourless glass which is greenish-blue in thick layers; 0·48 per cent. a light sea-green; 0·73 per cent. a bright sea-green; 1·23 per cent. a bright yellowish-green; 5·56 per cent. a deep yellowish-green, but still transparent; 8·23 per cent. a dark olive green, still transparent even in thick layers; 11·12 per cent. a dark olive green, but opaque in thick layers. The percentages stated were obtained by the analysis of test glasses, and therefore represent the amount of iron present in the finished glass.

As might be expected, the colours given by copper depend upon the conditions under which the glass is melted. A blue or green glass is obtained from copper compounds under oxidizing conditions and a ruby colour under reducing conditions. For green glasses the black or cupric oxide is used.

Chromium was discovered in 1795 in the Russian mineral crocoite, which is a lead chromate that has been used for colouring glass since the early part of last century. The name is derived from the Greek word *chrōma* (colour) and indicates that chromium compounds have vivid hues.

GREY

To produce grey or 'smoked' glass the colouring agents used are combinations of (*a*) cobalt, nickel, and uranium oxides, or (*b*) manganese, iron, and copper oxides. The glass may be of either the soda-lime or lead-potash type.

OPAL

Opal glasses fall into two main classes. First, that in which the opacifying agent dissolves, leaving the glass transparent while molten but causing it to become opaque upon cooling. Second, that in which the opacifier never wholly dissolves but remains very evenly and finely distributed throughout the molten metal. In the one type, the glass is quite transparent when gathered from the crucible and gradually becomes opal as it cools. In the other, the metal is already opal upon gathering but becomes more so as the temperature falls.

In most opal glasses the opacity is dependent upon the separation of either finely divided silica, or some metallic oxide, or both, from the mass of glass. The separation is assisted by the presence of fluorides and phosphates. A certain degree of opalescence may result from the separation of the fluoride (say as aluminium fluoride) or the phosphates themselves from the glass, but as a rule the batch is such that they remain combined as fluo-silicates and phospho-silicates, throwing the silica out of solution. The source of the opal colour in glass, therefore, may be either excess of silica, excess of a metallic oxide, e.g. of aluminium, tin, or antimony, or the presence of fluorides or phosphates.

Duval d'Adrian has sought to show that, by using the complex fluorides of silicon, boron, tin, zirconium, and titanium with the fluorides of the alkaline earths and heavy metals, and adding various mixtures of these to an ordinary glass batch, more satisfactory results are obtained than with simple fluorides.

Opal glass is being increasingly used for a wide variety of purposes. It is now commonly found in the form of illuminating globes and bowls, sheet glass, towel rails, imitation candle tubes for electric lighting, containers for pomades and other

druggists' sundries, and linings for electroplated articles.

ORANGE

According to Sir Herbert Jackson, the famous Chinese *sang-de-bœuf*, or oxblood, glazes were due to dispersed finely divided copper in amounts of the order of 0·5 per cent., the reducing conditions under which they were made preventing any tinge of green through the presence of cupric oxide.

PURPLE

The compounds of manganese are among the oldest colouring agents used in glass. Dralle and others have stated that the purple colour is produced by the tervalent manganese oxide, Mn_2O_3, in equilibrium with MnO. To secure a deep colour with manganese the founding has to be under oxidizing conditions, as reducing agents destroy the purple tint.

Two pieces of transparent glass of an intense purple colour were sent to the late Sir William Crookes from South America. They had been found on rubbish heaps at a high altitude and had been exposed to the action of the sun over a long period. The probable cause of the colour was manganese, which would be affected by the solar rays of short wavelength, present at an altitude of 4,000 metres but absent at sea-level owing to atmospheric absorption. The colour had penetrated the whole mass, but disappeared when the glass was reheated to softening-point. By exposure to radium rays the colour could quickly be reproduced.

RED AND RUBY

Copper oxide in the cuprous form, melted under reducing conditions, gives an excellent ruby. If a copper ruby is reheated slowly for some time the particles of copper aggregate and become visible to the naked eye, giving what is known as an aventurine glass. This type of glass was first made at Murano, the name 'aventurine' being from the Italian *avventurino* (chance), indicating its accidental discovery. It has been described as a semi-opaque glass filled with golden yellow spangles.

On the rare occasions when a gold ruby glass is made today it is generally prepared from a soft lead batch containing an excess of antimony and arsenic. The gold is added in the form of a solution of gold chloride, in the proportion of 1 oz. of metal to 200 lb. of batch.

Selenium was first isolated in 1817 by Berzelius, who used the mud of sulphuric acid plants as his raw material.

Although selenium is now being used more and more as a source of red colour in glass the colour is difficult to retain, because if great care is not taken the selenium has a strong tendency to volatilize.

VIOLET

Colours ranging from violet to purple can be obtained by adding less than 1 per cent. of titanium dioxide (TiO_2) to the batch mixtures of certain borosilicate or phosphate glasses.

YELLOW AND AMBER

It is believed at present that no single element can be used to isolate spectral yellow in glass. Glasses of varying shades of yellow are, however, produced by means of cadmium, silver, sulphur, and uranium.

Carbon is very commonly used in the manufacture of yellow glasses, being introduced in the form of coke, graphite, or anthracite. It is the sulphate-containing impurities in the carbon which are the true source of the colour. This was demonstrated among others by Splitzerber, who in 1839 melted two carbon-containing batches, the first of which had 1·75 per cent. of sodium sulphate but the other none, and only the former developed a yellow colour. Again, in 1865, Pelouze obtained similar results.

In the making of amber glasses it is usual to employ a mixture of sulphur and charcoal as the colouring material. The batch must of necessity be melted in a reducing atmosphere. Experiments by Fenaroli and others led to the conclusion that the elements of the group giving yellow colours are effective in colouring glasses only when they are present as polysulphides, polyselenides, or polytellurides.

It was in 1789 that Klaproth isolated a new element, uranium, from the mineral pitchblende. He obtained sodium uranate as a bright yellow precipitate, which soon came to be used as a colouring agent for glass and glazes. When available, uranium can be used with antimony to give a stable yellow in glasses containing lead.

ACKNOWLEDGMENTS

Figures 1, 2, 3, and 5 from *Stained Glass of the Middle Ages in England and France*, by Hugh Arnold. Paintings by Lawrence B. Saint. (A. and C. Black.)

Figure 7 from *English and Irish Glass*, by W. A. Thorpe (The Medici Society).

Figures 8 and 9 from *Glass*, by Edward Dillon (Methuen & Co.).

Plastic optical materials

D. STARKIE

Although the possibility of using transparent plastic materials in optics has long been recognized, the moulding of optical components presents much difficulty, owing largely to the tendency of the material to shrink away from the mould. This article includes an account of a method by which the surface of an original moulding can be built up so that the contours of the mould are faithfully reproduced. The method is of particular interest in connection with the construction of television receivers with relatively large screens.

From the time when plastics were first used in industry some of the transparent varieties appeared to be of value as possible new optical materials. A number of their physical properties were clearly favourable for optical work, e.g. low density, high light transmission, an outstanding toughness and resistance to severe thermal shocks, and an ability to reproduce faithfully the surface of a mould. On the other hand, when compared with glass, the transparent plastics have a relatively low resistance to scratching of the surface, less rigidity, and a relatively high coefficient of thermal expansion. Further, the range of plastic materials suitable for optical work is at the moment limited, although new transparent plastics providing an adequate range of optical constants will doubtless be synthesized and become available commercially. In attempting to assess the value of plastic materials to the optical industry, these advantages and disadvantages must be carefully considered.

THE VALUE OF PLASTICS AS OPTICAL MATERIALS

Two plastic optical materials are readily available in Britain, namely polymethyl methacrylate and polystyrene, of an appreciably higher purity than that normally associated with the commercial products. As a result of this increased purity, both materials have a relatively high softening-point and an improved craze resistance, and the development of new methods of manufacture and treatment has resulted in a freedom from strain and an optical homogeneity equalled only in the finest optical glass. The optical properties of these two materials are such that they can be used satisfactorily for achromatic lens systems. As they are pure chemical substances their refractive indices are unaffected by variations in the method of manufacture, and it is easy, therefore, to maintain the values accurate to 0·0001 from batch to batch—a factor of importance in precision optics.

The low density of the materials when compared with glass is attractive in that when plastic components are used in an optical instrument—particularly one containing massive prisms—a considerable saving in weight results. Their resistance to mechanical and thermal shocks has already made plastic optical materials valuable during wartime, and has made possible certain applications where glass is too brittle to use.

Extra care in designing an optical instrument can offset many of the disadvantages of the materials. The reduced rigidity calls for more attention in mounting if stresses causing distortion are to be avoided, although by reason of their low density plastic optical components, as compared with glass, require reduced mounting pressures to obviate displacement. The low scratch-resistance of optical plastic materials has tended to be over-emphasized, for a scratch on their surface is simply a depression with no broken edges, and the actual light-scattering area is appreciably less than with a scratch on glass. The relatively high thermal expansion again calls for care in design and mounting, and in extreme cases thermal compensating devices may be incorporated in the instrument. If the instrument is intended for use at very high temperatures it will be impossible to use plastic optical components, but a method of manufacture referred to as the 'surface-finishing' process, which has been developed recently [1] and will be described later, enables plastic optical components to be produced which are stable at temperatures up to 100° C.

It is, however, on the ability of plastic optical materials to reproduce faithfully the surface of a mould that the main interest has been centred, since it is this property which will enable the materials to make a new and extremely important

contribution in the field of applied optics. Given a method of highly accurate reproduction from a master mould, plastic optical components can be made rapidly and cheaply. No special difficulties in making large-diameter components will be encountered, and in consequence the serious difference of price existing between large and small components made in glass will not be paralleled. Moreover, components with non-spherical or aspheric surfaces can be made at a cost sufficiently low to enable them to be used for all optical applications, once the moulds have been prepared. The ability to produce optical components with aspheric surfaces at a relatively low cost represents the chief attraction of plastic optical materials.

ASPHERIC OPTICAL COMPONENTS

It is well known that a lens, the surfaces of which are portions of a sphere, suffers from spherical aberration. With a single lens forming an image of a point source of light, the aberration causes a spreading of the image over an area instead of a concentration of the light rays to a point. If accurate concentration of the light rays to a point is to be obtained by a single lens it will have to refract the rays striking its central portion more strongly, and the rays near its perimeter less strongly, than occurs in using surfaces of spherical form. For this reason the stopping down of a lens, i.e. the screening-off of the rays from the outer edges, produces a sharpening of the image, but of course at the expense of its intensity. If the full aperture of a single lens is to be used and an accurate point image is to be obtained, it is necessary to depart quite appreciably from surfaces of spherical form and to use lenses which are flatter near the edges and steeper at the centre than on a sphere.

It is possible to make some reduction in the amount of spherical aberration in a system of lenses by selecting the shapes of the individual lenses so that the spherical aberration introduced by the negative elements is as nearly as possible equal and opposite to that introduced by the positive ones. Many ingenious, but often expensive, ways of arranging lenses with spherical surfaces in a system to reduce spherical aberration have been devised, but they unfortunately impose added restrictions in the design of certain types of optical system. Further, any introduction of additional lenses to the system adds to the losses by reflection, owing to the extra surfaces. There are certain applications where it is impossible to obtain the requisite performance using lenses with spherical surfaces, and where only aspheric surfaces can be entirely successful.

Unfortunately, the usual grinding and polishing methods of making glass optical components normally allow only spherical or flat surfaces to be worked, and the sole satisfactory way of making surfaces other than these in glass is by laborious hand-figuring of small portions of the surface until the whole area of the component has been completed. The cost of hand-figuring an optical component in this way is very high indeed, for many days of patient work by a highly skilled craftsman are involved. The use of aspheric optical components has therefore been limited to applications where cost is of secondary importance only. Many attempts have been made to produce aspheric optical components at economic prices, e.g. by using machines of special design to work the surfaces automatically, but the impossibility of constructing machines capable of working to, and maintaining, the requisite degree of precision has prevented entirely satisfactory results from being obtained.

THE 'SURFACE-FINISHING' METHOD OF MANUFACTURING PLASTIC OPTICAL COMPONENTS

Two methods of making plastic optical components by reproduction from a mould are already in operation on a manufacturing scale. The first [2] is moulding the material by compression between the two halves of an optically worked stainless steel mould, the material having first been 'preformed' to the approximate shape of the interior of the mould by machining. The second [3] is by polymerization, in which the solid polymer component is cast from the liquid monomeric form, in the presence of a suitable catalyst, inside an optically worked glass mould. Optical components made by both these methods of manufacture (which have been in operation for a number of years) have found a variety of uses.

Details of the new 'surface-finishing' process for the manufacture of plastic optical components by reproduction from a mould have been published recently. This method promises to be of importance in that it gives an extremely accurate reproduction of the interior of an optically worked mould, while the resulting optical components are entirely free from strain and are therefore stable at high temperatures.

The main ideas on which the 'surface-finishing'

FIGURE 1 – *Two aspheric lenses with their respective moulds.*

FIGURE 2 – *An 8 in. diameter optical system for a domestic television projection receiver, and an 18 in. diameter system for television projection in a cinema.*

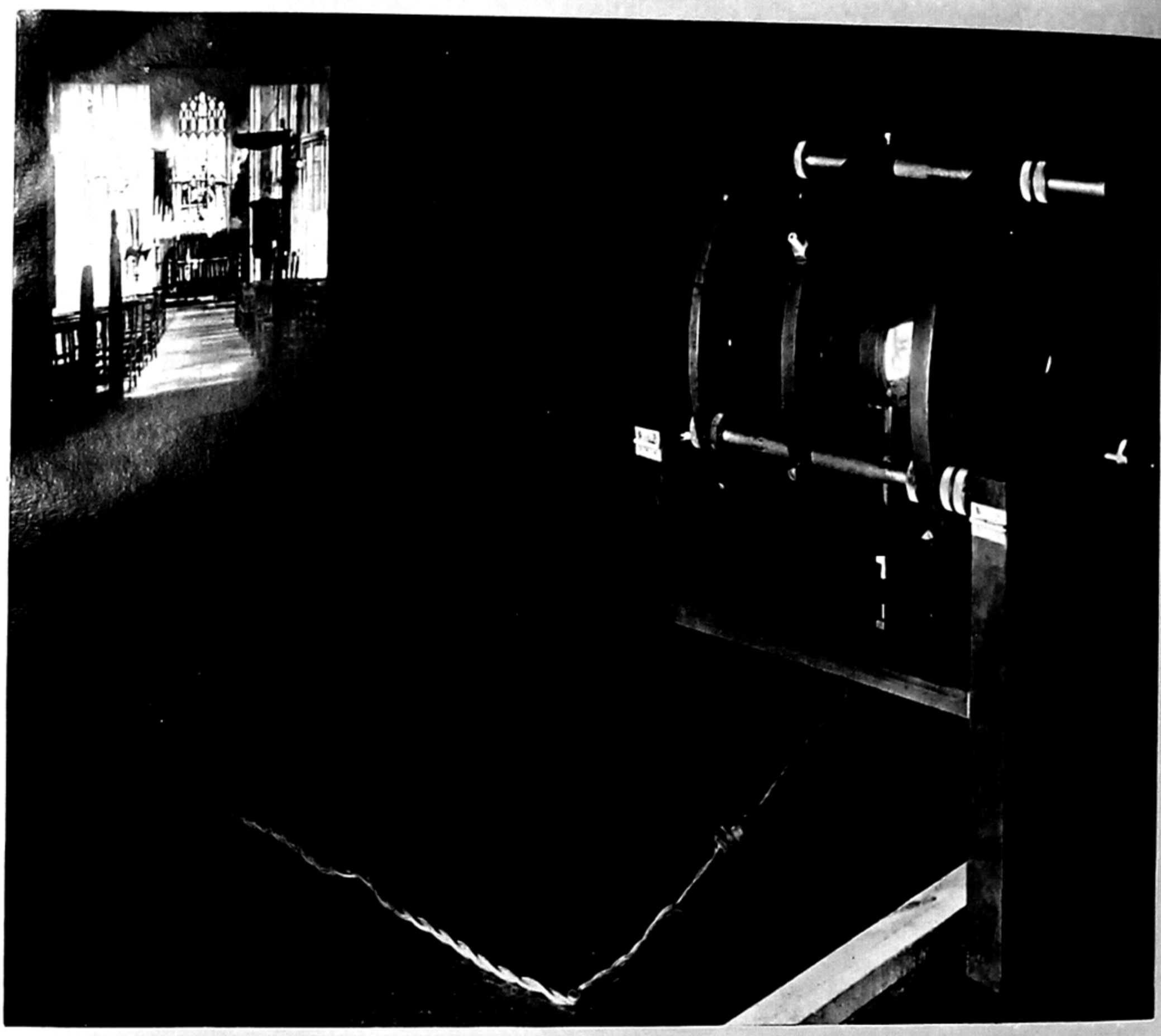


FIGURE 3 – *An 8 in. diameter television projection system projecting a picture on to a separate screen.*

process was based were (*a*) to make a strain-free preform of an optical component by some known method, and then (*b*) to build up on the surface of this preform a thin skin of the same material inside an optically worked mould until its surface made optical contact with the mould at every point. After stripping from the mould, the optical component would then be ready for immediate use. It was assumed to be essential that the use of pressure throughout the reproduction process should be avoided if perfectly strain-free, and hence stable, optical components were to be obtained.

After considerable investigation, straight polymerization, or casting from the monomeric state, in a mould, such as is used in one of the existing processes of manufacture already mentioned, was selected as the method of making the preforms. For a variety of reasons, and particularly with a view to easy operation on a manufacturing scale, polymerization by exposure to light, with a suitable photo-catalyst present in the monomer, was adopted in preference to the more usual heat polymerization for making the preforms. A considerable portion of the investigation has been concerned with the discovery of photo-catalysts and satisfactory light-polymerization conditions. There is a large contraction in volume with all the most desirable optical plastics on changing from monomer to polymer, and this increases the difficulty of making an accurate preform; but the contraction can be reduced to some extent by carrying out a partial polymerization of the monomer before filling the mould. The liquid which finally goes into the mould has a high viscosity, and the degree of polymerization of the liquid which can be allowed is limited by the fact that it must flow sufficiently easily to fill the mould. The final contraction inside the mould is taken up by allowing the two halves of the mould to be drawn together during the polymerization. When polymerization is complete, the mould containing the preform is chilled suddenly, and the two become separated owing to the fact that they do not contract equally. The preform, as it leaves the mould, is surrounded by 'flash,' which is machined off,

after careful optical centring, in a lathe fitted with a vacuum chuck. The last stage in the preparation of the preform is a careful annealing to remove all traces of strain which may have been introduced by firm attachment to the surfaces of the mould during polymerization.

The difficulty in controlling the relatively large contraction in volume on polymerization makes it practically impossible to obtain first-class optical accuracy in the preform, and if the latter is placed back in the mould it will be found to have departed slightly from the true form. These minute spaces are filled up, therefore, by polymerizing a thin film of the same material on the surface of the preform, the film being so thin that its contraction on polymerization can be accurately controlled. Great care in carrying out this operation is required, and an exact routine procedure has been worked out. After stripping from the mould, the finished optical component is given a final edging on a lathe fitted with a vacuum chuck.

If optical mirrors are being made, a reflecting layer of aluminium is deposited on them by evaporation in a vacuum chamber, and the same apparatus can be used for coating lenses with non-reflecting films.

All the moulds used for the 'surface-finishing' process are made of glass. Glass was selected as being the hardest suitable material available in sufficient quantity. Since part of the reproduction process is by light-polymerization a transparent mould material is, of course, required.

The time necessary to make an optical component by the new process is long, although the actual handling time is short. A suitably equipped factory would contain mechanical conveyors to carry a large number of moulds through the various stages of the process, and it is hoped that such a unit will be in operation in Britain in 1948.

APPLICATIONS REQUIRING ASPHERIC OPTICAL COMPONENTS

The 'surface-finishing' process is to be applied in the first place to the manufacture of aspheric optical components, and the workers engaged on the development of the process have had to investigate both the design of such optical systems and methods of working aspheric moulds. Much progress has been made in each direction. As regards the working of the moulds, it was accepted from the beginning that hand-working methods would have to be used, and the main concentration was on devising new methods of testing the exact contours of the mould at all stages of its preparation, and on providing mechanical devices which would be helpful to the skilled craftsmen engaged on the work. New mechanical methods of testing which can be operated by the optical worker himself are used in the early stages of the mould-making, while optical tests carried out by experienced men are employed in the final stages. Complicated aspheric moulds are now produced at a much higher rate than was anticipated in the early days of the investigation. Figure 1 shows two aspheric moulds, together with lenses made from them.

An application for which an aspheric optical system is essential is television projection. In view of the urgency with which television projection systems are likely to be required, the 'surface-finishing' process has been applied primarily, up to the present, to the preparation of a range of prototypes for this application. It is generally agreed that the picture on the curved end of the cathode-ray tube which is provided by the present domestic television receiver is by no means satisfactory for viewing by a number of people, and that a much larger, flat picture is desirable. A sufficiently large cathode-ray tube would be bulky and expensive, and a much more attractive way of providing a picture of the desired dimensions is to generate a high-intensity television picture on the end of a small tube and to project an enlarged image of it on to a separate screen by means of a suitable optical system. Unfortunately the brightness of the cathode-ray tube picture in a domestic receiver is necessarily limited, and to give a satisfactory screen picture an optical system of large light-gathering power is required. A system capable of meeting all requirements is one that was designed originally for use in an astronomical telescope [4] and is usually referred to as a Schmidt system. In applying such a system for television projection, the small cathode-ray tube faces a concave mirror of large aperture which collects and projects beyond the tube a considerable percentage of the light from the television picture, while an aspheric corrector plate situated at the centre of curvature of the mirror corrects the spherical aberration of the mirror and redirects the rays of light accurately to their appropriate positions on the screen. A drawing of a Schmidt system used for television projection is shown in figure 4. With this combination of mirror and corrector plate, f numbers of 0·75 can be obtained without difficulty, even though the cathode-ray tube screens off the centre

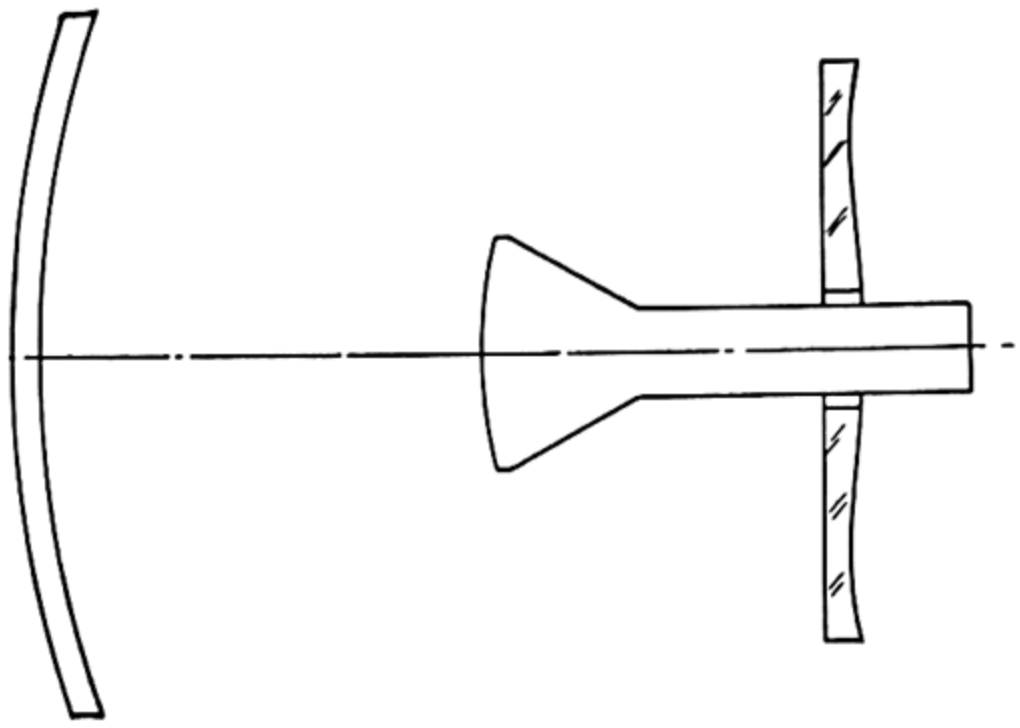


FIGURE 4 – *Diagram of a Schmidt system used for television projection.*

of the system. Provided that the mirror and corrector plate are of sufficient accuracy, a bright, sharply defined screen picture can be obtained from a relatively low-intensity cathode-ray tube picture. Once the moulds have been prepared, both mirror and corrector plate can be made by the 'surface-finishing' process at only a fraction of the cost of the same system in glass.

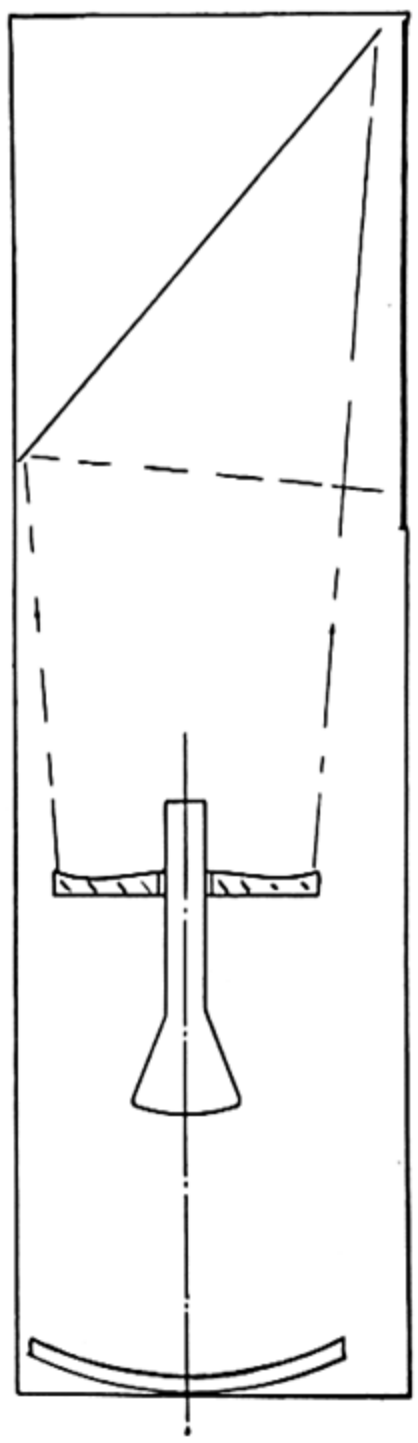


FIGURE 5 – *Arrangement of Schmidt system with 45° plane mirror in a television receiver.*

Up to the present, Schmidt systems for two sizes of projection cathode-ray tube for use in domestic receivers have been made by the new process. One system, containing an 8 in. diameter mirror, is for use with a $2\frac{1}{4}$ in. diameter cathode-ray tube, while the other, with an 11 in. diameter mirror, takes a $3\frac{1}{2}$ in. diameter tube. Both systems have a focal ratio of *f*/0·75, have a throw-distance from mirror to screen of 40 in., and give a screen picture measuring 15 in. by 12 in. Figure 5 shows how, by the introduction of a plane mirror at an angle of 45° to the light beam and a translucent screen, this 'throw-distance' of 40 in. can be accommodated in a television cabinet of reasonable dimensions. Figure 3 shows the 8 in. diameter system in operation, projecting an actual picture on to a separate screen.

There is also a demand for full-size television projection in cinemas. Here the life of the cathode-ray tube is less important than in the domestic receiver, and expensive auxiliary equipment can be installed, so that a cathode-ray tube picture of much greater brightness can be provided. This greater brightness in the tube picture is, however, offset by the fact that the projected image covers a very much greater area on the screen, and an optical system of large light-gathering power is again required. A Schmidt system of *f*/0·8 containing an 18 in. diameter mirror and with a throw-distance of 42 ft. has been made by the 'surface-finishing' process. This system, which is being used experimentally in a cinema, is giving a picture 10 ft. by 8 ft., and the brightness of the screen picture is equal to that normally obtained in a cinema by projection from a film. An optical system of still greater dimensions for use in the largest types of cinema is now being prepared. The comparative sizes of the 18 in. diameter cinema system and the 8 in. diameter domestic system can be judged from figure 2.

Although the 'surface-finishing' process has so far been applied primarily to optical systems for television projection, a wider field of application has been borne in mind. Prototype aspheric magnifying lenses which allow an operator to inspect tiny manufactured parts (using both eyes) without experiencing any sign of eyestrain have already been made. Projection systems of large light-gathering power for applications requiring either high-intensity projected pictures for viewing in brightly illuminated surroundings, or reasonable picture brightness from low-wattage lamps, are being designed, and practical trials will be carried out in the near future. These applications include filmstrip projectors for educational and publicity purposes, new types of signals and indicating devices for railways, micro-film projectors, and special projectors for use in film studios. All these systems and components, which may be required in substantial quantities, are particularly suitable for manufacture by the process of 'surface-finishing,' which will allow plastic optical materials to play an important part in the field of applied optics in the future.

REFERENCES

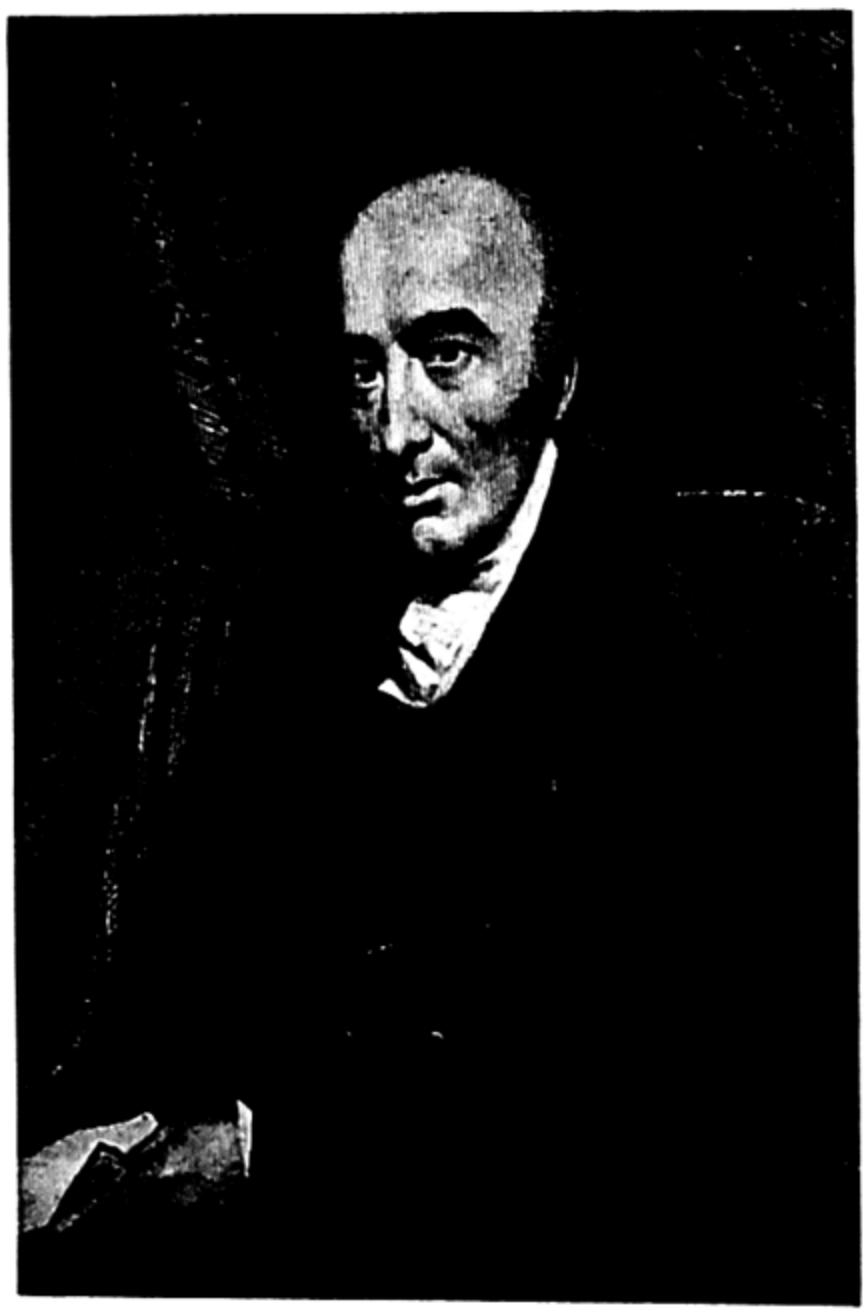
[1] *British Plastics*, **XI**, March 1947, p. 117.
[2] *Ibid.*, **XVIII**, May 1946, p. 219.
[3] *American Plastics*, **IV**, May 1946, p. 27.
[4] *Mitteilungen*, Hamburger-Bergedorf, **VII**, No. 36, 1932.

The story of malleable platinum

M. SCHOFIELD

The intractability of platinum long obscured its usefulness, and to the early Spanish miners it was nothing more than a tiresome impurity, to be discarded and dumped into the rivers of South America. Realization of the valuable properties of platinum was followed by a long struggle to render the metal malleable so that it could be fabricated into useful articles. The subsequent extensive use of platinum for laboratory and industrial equipment, jewellery, dental accessories, and other articles was a first result of pioneer work in powder metallurgy.

The history of platinum, otherwise *platina* or 'white gold,' may be divided into two parts, each of which is as absorbing as that of any other metal. There is the general history of the element, well known and set in order: a tale opening with such names as that of Julius Caesar Scaliger who, in 1557, made a first reference to a metal found between Mexico and Darien, a metal 'which no fire nor any Spanish artifice has yet been able to liquefy.' Then there is the second section, hardly as yet fully knit together: a section dealing with the making of malleable platinum, with a process which put into service a metal of which whole cargoes had lain idle as useless. This second part is indeed compelling, for it brings on the scene so many chemists of Europe: men like Scheffer, Macquer and Baumé, Achard and Lavoisier, and the less-known Chabaneau, with a goldsmith or two like Jeanety of Paris. Most important of all, it brings in William Hyde Wollaston, Thomas Cock, Richard Knight, Johnson, and Matthey to finish the early history of platinum fabrication on a triumphant note for the British school. But even today there are gaps and disjointed pieces in this story, particularly as regards the making of large platinum vessels for the concentration of vitriol. Had Wollaston sufficient elbow-room wherever he worked to construct those platinum vessels which the *Dictionary of National Biography* maintains he made himself? How much knowledge did he gain from Thomas Cock? Certain it is that the platinum still or boiling-vessel used by Sandemann was not made by Johnson, Matthey and Company as some historians have suggested, for, as D. McDonald [1] has pointed out, in 1809 P. N. Johnson was but sixteen years old and George Matthey had not been born.



William Hyde Wollaston, M.D.

In studying the fabrication of platinum, distinction must be made between early workers using, intentionally or otherwise, an alloying element to render platinum more susceptible to mechanical working and forging, and the first workers beginning the powder metallurgy of pure platinum. Among the latter Wollaston was a dominating figure. Long before Don Antonio de Ulloa, a member of the 1735 French and Spanish expedition dispatched to measure a degree of meridian at Quito, published his *Historical Account of the Voyage to South America*, primitive Indians had fished out from the Pinto river some water-worn nuggets and grains of this 'free' metal (free for anyone to take), and fashioned it into ornaments. According to Bergsøe [2] these Indians, in fashioning their nose-rings, could not have melted platinum. Not a single cast object was found, nor was any solder used. All was done by welding and cold hammering, using charcoal and the blowpipe to bring the grains into a coherent form. But there was 30 per cent. of gold present to seal together the platinum grains before the mass was sintered and then made homogeneous by hammering and

heating. Such alloying of platinum and gold has persisted through the centuries right up to the present day: a modern example is the platinum-gold spinneret to which rayon producers have reverted after tantalum—rival to platinum—failed to stand the test. Yet platinum was to the gold-miners of the Choco district of Columbia what tungsten was to the tin-miner, or nickel ('Old Nick's metal') was to copper-miners. Gold mines were abandoned because of it, and, since the Spaniards were not averse to using gilded platinum as counterfeit, their government banned its export and ordered the metal to be dumped into rivers.

Though the ship bringing back De Ulloa was captured by the British Navy, the Admiralty 'unanimously and with pleasure' returned to him his scientific manuscripts, adding that they were 'not at war with the arts and sciences or their professors.' Hence his historical account was saved, and after its publication just two centuries ago all sorts and conditions of chemists in Europe were attracted to 'this obdurate body.' De Ulloa went on to develop the Almaden quicksilver mines, leaving it to Sir William Watson and William Brownrigg to introduce platinum. Brownrigg [3], whose *platina* from Jamaica had been given him by a relative, Charles Wood, told of its high melting-point and its refractoriness (noted by Wood), and he believed the Spaniards had melted it and cast it into sword-hilts, buckles, and snuff-boxes. Such first dabblings with platinum were extended by the Swede Scheffer [4], who in 1752 succeeded in fusing a sample of 'white gold' (obtained from Watson in London) by the use of arsenic; and by Lewis [5], whom Scheffer anticipated and who published his observations in the *Philosophical Transactions*. In 1772 von Sickingen rendered platinum malleable by alloying it with gold and silver. He also dissolved it in *aqua regia*, added ammonia, ignited the precipitated ammonium platinichloride, and hammered the fine platinum to effect cohesion.

Such an important step towards producing malleable platinum by way of the metallic powder was the practical realization of an idea of Antoine Baumé, who suggested that platinum could probably be forged and welded as iron had been worked among the ancients. In mentioning Baumé one must give credit to several Frenchmen, chemists and others, who made persistent efforts to harness the metal. Thus M. de l'Isle [6] in 1770–4 used the ammonium platinichloride method to obtain finely divided platinum, and agglomerated this to the malleable form. De Morveau [7] tried alloying with lead as well as the arsenic method. Achard, father of the beet-sugar industry, also used arsenic and is said to have made the first platinum crucible. There was also the Abbé Rochon [8], director of the Marine Observatory at Brest, whose method was to purify platinum grains 'in a strong fire' with nitre and sulphate of soda, adding one-eighth part of the tin–copper alloy used for common specula, exposing the mixture to 'violent heat,' and fusing it before pouring it into a mould to give a large speculum weighing 14 lb., with a diameter of 8 in. and a focal length of 6 ft. To continue the part played by Frenchmen, Lavoisier [9] in his *Observations sur le platine* told how Baumé tried lead and bismuth as alloying metals; others used arsenic, which was removed by vaporizing on subsequent heating; and Rochon used copper and tin capable of being dissolved in nitric acid after reducing, leaving platinum as a black powder. Lavoisier doubted whether this could be used in large-scale work, and then referred to Jeanety as the man worthy of most merit. The jeweller Jeanety of Paris, receiving some platinum ingots from Chabaneau, made platinum snuff-boxes, a coffee pot shown by Lavoisier to the Academy, watch chains, and platinum buttons. Berthollet and Pelletier credit Jeanety with perfection in platinum-working by alloying with arsenic in a crucible, obtaining a button, breaking this up and treating the product with white arsenic and refined potash, and finally vaporizing the arsenic—an eight-day operation. To Jeanety, let it be noted, came the *savants* to buy platinum crucibles and the Academy to get bars of platinum.

Jeanety's platinum was supplied by Pierre François Chabaneau, that versatile yet almost unknown French chemist, who deserves a paragraph to himself. While Jeanety was the first to make fairly pure platinum sponge in quantity and to fabricate it at a white heat, he continued with his arsenic when he failed to discover Chabaneau's method. Chabaneau [10], a native of Dordogne, was expelled from his theology school and took a mathematical teaching post at Passy, where he studied by fire-light for the next day's teaching. It was while he was giving some public lectures that certain Spanish members of the audience were attracted by him and persuaded him to go to Spain. So we hear of Chabaneau going to Vergara to teach physics, collaborating with de Elluyar of tungsten fame, and being installed by Charles III in a science chair at Madrid, with a royal palace as lodgings and a valuable library and well-equipped laboratory at his disposal. At this period Spain suddenly

realized that her South American platinum, hitherto despised, was an asset. It was turned over *en masse* to Chabaneau, thus beginning what has been called 'the platinum age' in Spain. Chabaneau had a difficult problem: chemistry was not yet sufficiently advanced to bring the recognition that platinum could be malleable at times and brittle when iridium was present, and that the original ore contained a number of metals like gold, mercury, lead, copper, and iron as well as those of the platinum group. 'Away with it all! I'll smash the whole business!' cried Chabaneau on more than one occasion as he threw his apparatus out of doors in a tantrum. 'You'll never again get me to touch the damned metal!' Yet it was a different Chabaneau who one day placed on the table of the Marqués de Aranda a 23 kg. ingot of malleable platinum in the shape of a 10 cm. cube—which the Marqués found surprisingly heavy. Chabaneau and his fellow-worker Cabezas made utensils and ingots in their prosperous business, and produced platinum crucibles for the use of Joseph Louis Proust. The king would often come to the laboratory to watch Chabaneau at work, but what was more important was the grant of a life pension and letters patent of 1783 establishing priority for Chabaneau's method.

While the goldsmith Jeanety continued to supply platinum apparatus from the metal processed by the Scheffer-Marggraf-Achard method, involving the use of arsenic and its subsequent volatilization, and while Count Apollos Moussin-Poushkin [11] in 1805 was using a mercury amalgamation method with the removal of mercury by the same means, the English school of platinum fabrication was developing. Richard Knight [12], for example, published a *New and Expeditious Process for rendering Platinum Malleable*. This involved compression of ammonium platinichloride into a hollow conical crucible with cover, the reduction to platinum at a strong white heat in an air furnace, and the hammering-in of a red-hot stopper to yield a platinum button which was then hammered and further heated. There was also Thomas Cock [13], who reduced platinum to a sponge in the platinichloride process and followed this by compression in an iron mould with a screw press for removing air. When volatiles had been driven off at a white heat, the platinum was hammered 'in all directions' on an anvil, and after a borax-flux treatment the working was repeated. Cock was a brother-in-law of P. N. Johnson and worked in William Allen's laboratory at Plough Court, London. He is believed to have worked on platinum from 1800 to 1809; he then disappeared for a time and later is heard of helping his brother-in-law and leaving a son to carry on the business. He seems to have communicated his method to Wollaston at Allen's request [14] and to have rediscovered Chabaneau's process—as did Knight (the latter, according to one report, being the first to fabricate large sheets of pure platinum free from flaws [15]).

Yet among the early platinum-workers William Hyde Wollaston stands out as the most prominent figure. There is a hint that Wollaston [16], after seeing Cock's work, took away some ideas which he did not acknowledge—ideas extra to whatever Cock told him. Whatever the truth of this may be, his own contribution is so great, as D. McDonald [17] remarks, that anything Cock provided could have been only a minor part. Wollaston, working in his secret laboratory, was the first to fix the composition of native platinum, and was the collaborator of Smithson Tennant in the study of palladium, osmium, iridium, and rhodium. He knew the exact proportions of *aqua regia* mixtures which would leave iridium undissolved, and how to expel volatiles from the platinichloride without allowing the platinum particles to adhere. But he was a business man and made a fortune of £30,000 from platinum fabrication, using it as a means of retiring at 34 to devote himself to scientific studies. He seems to have obtained platinum on a fairly large scale, fabricated it into laboratory ware (thus making this country independent of manufacturers abroad), and then turned his attention to making those large boilers for sulphuric acid which could not have been made by Johnson and Matthey. Wollaston was secretive and published nothing until, just before his death, he decided to broadcast his method in the Bakerian Lecture [18] of 1828. 'As, from long experience, I probably am better acquainted with the treatment of Platina, so as to render it perfectly malleable, than any other member of this society . . .' —so he opens his dissertation in which he tells how he avoided dissolving iridium by dilution of the *aqua regia*; how he rubbed the finer grey platinum powder in his hands and the coarser in a wooden pestle and mortar so as to avoid burnishing the particles. He washed the powder by levigation, made a mud of specific gravity 4·3 with water, compressed this to a cake of specific gravity 17–17·7 in a conical brass barrel-mould greased with lard, and used a lever press in place of Cock's screw press. In Wollaston's hands every part of the process was subjected to minute care and attention. He used first a charcoal fire to remove

moisture and grease and give finer cohesion, and then a wind furnace fired with Staffordshire coke to effect cohesion before hammering, reheating, and forging. As Thomas Thomson [19] put it, 'Wollaston first succeeded in reducing platinum into ingots in a state of purity and fit for every kind of use.' With his warnings against work-hardening the powder, Wollaston was an early powder-metallurgist, a pioneer in that struggle which has given us tantalum, tungsten, molybdenum, and niobium.

Wollaston's success had its fruits both in the laboratory and on a large scale. Instead of relying on France and Jeanety's followers for apparatus, chemists like Berzelius would apply to London for malleable platinum, and later, after Wollaston's method was published, were enabled to renew platinum apparatus made by less satisfactory methods.

On the commercial side it was for concentrating vitriol in stills or boilers that malleable platinum was brought to prominent use. It was Sandemann, a chemist member of the British Mineralogical Society, who maintained a small chemical works at Thames Bank and used such large boiling vessels, although Richard Farmer seems to have been the first sulphuric-acid maker to adopt this process, according to Knight's *English Encyclopaedia* of 1857 [20]. At his works on Kennington Common, Farmer engaged Wollaston to supervise the construction from his own platinum of a 323½ oz. troy vessel at a cost of £300; other vessels followed in 1820 totalling 828 oz. and costing £685. Wollaston charged for the weight of platinum supplied and for the workmen's wages, his own services being free. Sandemann in December 1809 had a vessel made of deep circular form, the weight being 423 oz. and the capacity 300 lb. of sulphuric acid, for use under a lead-chamber plant. This was the vessel previously referred to, which could not have been made by Johnson and Matthey.

With the death of Wollaston other makers of malleable platinum were left to carry on in London, Paris, and Russia. In France there were Desmoutis and Quennessen. In London were P. N. Johnson, founder of Johnson, Matthey and Company, who worked with Cock, his brother-in-law, with W. J. Cock the son, and others in business as Johnson & Sons. Johnson and Matthey soon won first place among such producers, and kept it through the agency of George Matthey and John Scudamore Sellon, having access to the considerable resources of Russia for their raw material. Half-way through last century the British concern had captured the world market, all this following a fruitful collaboration between Matthey and Sellon on the one hand and Deville and Debray [21] on the other. In 1861 platinum boilers for treating sulphuric acid were shown at a London exhibition, these being made by a 'patent autogenous soldering.' More than 160 concentrating vessels of from 20 to 160 gallons' capacity had been made by the old system of gold-soldered joints, but the patent soldering used the oxy-hydrogen blowpipe method as first described by Robert Hare before the Chemical Society of Philadelphia in 1801. In 1878 at the Paris Exhibition [22] Johnson and Matthey exhibited platinum ware, Deville and Debray's melting-process having replaced the compression-hammering method in producing such large ingots as were then prepared. 'Sponge' ingots are superior to unalloyed melted metal, provided the sponge is pure and that all the precautions given by Wollaston are observed. Such is the early story of malleable platinum. Further important advances in the metallurgy of the platinum metals have of course been made since those pioneering times, but they lie outside the scope of the present article.

REFERENCES

[1] McDonald, D. Private Communication.
[2] Bergsøe. *Nature*, 1936, **137**, 29; and 1937, **139**, 490.
[3] Brownrigg. *Ann. Phil.*, 1817, **6**, 321–38, 401–17.
[4] Morin, C. *Le Platine* (1758).
[5] Lewis. *Phil. Trans.*, 1754–5, **48**, 313–38, 638–89; and 1757, **50**, 148–66.
[6] de l'Isle. *Ann. de Chim.* 1792, **14**, 20.
[7] Morveau. *Ibid.*
[8] Rochon. *Phil. Mag.*, 1798–9, **2**, 19.
[9] Lavoisier. *Ann. de Chim.*, 1790, **5**, 137.
[10] Howe, J. L. *Chem. News*, 1914, **109**, 229.
[11] Moussin-Poushkin. *Phil. Mag.*, 1804, **20**, 76.
[12] Knight, Richard. *Ibid.*, 1800, **6**, 1.
[13] Aikin. *Dictionary of Chemistry*, 'Platina.'
[14] Allen. *J. Chem. Soc.*, 1867, **20**, 395; *Proc. Roy. Soc.*, 1867–8, **16**, xxii–xxv.
[15] Wollaston. *Popular Science Monthly*, 1914, **84**, 64–70.
[16] Knight. *Engineering Encyclopaedia*, 1857, Biographical Section, **6**, 794.
[17] McDonald, D. Private Communication.
[18] Wollaston. *Phil. Trans.*, 1829, **119**, 1.
[19] Thomson, T. *Hist. of Chem.* (1831), 216–17, 237, 247, 292, 297.
[20] Knight. *English Encyclopaedia* (1857), Vol. 6, 794.
[21] McDonald, D. Private Communication.
[22] *Chem. News*, 1878, p. 43.

The metabolism of nitrogen in soil

J. H. QUASTEL

From the bland assurance and circumstantial detail with which many elementary textbooks present the 'nitrogen cycle,' students might be pardoned for believing that the problem had been solved once and for all. Professor Quastel has a very different story to tell. He shows that the study of nitrogen metabolism in soil is still in its comparative infancy, and that while many of the basically significant facts have been elucidated there are very numerous phenomena of great interest—and great difficulty—yet awaiting full investigation.

Nitrogen metabolism in soil covers the vast sequence of chemical changes undergone by the nitrogen molecule in biological processes taking place in soil, from its initial fixation until its final liberation into the atmosphere. The main processes comprising this cycle of changes are as follows:

1. *The transformation of atmospheric nitrogen by soil micro-organisms into substances nourishing microbe and plant.* This process is generally known as biological nitrogen fixation, and is accomplished largely by two sets of organisms, one consisting of the root-nodule bacteria living in symbiosis with certain leguminous plants, and the other consisting of organisms living in the soil independently of plants.

2. *The transformations in soil of organic nitrogen compounds arising from autolysis of all forms of biological material, or from the excreta of animals, or from the products of metabolism of living soil organisms, into ammonium ions.* These processes are accomplished by a great variety of soil micro-organisms which, while developing aerobically or anaerobically on organic nitrogen compounds, produce ammonium ions as part of their metabolism; or they may be brought about by the action of hydrolytic or oxidizing enzymes present in soil micro-organisms, whether they are proliferating or not.

3. *The conversion of ammonium cations into nitrite and nitrate anions.* This process is generally referred to as soil nitrification, and is accomplished largely by two groups of organisms, *Nitrosomonas* (also *Nitrosocystis* and *Nitrosospira*), which forms nitrate from ammonium ions, and *Nitrobacter* (also *Nitrocystis* and *Bactoderma*), which converts nitrite ions into nitrate ions.

4. *The reduction of nitrate into nitrite and finally into ammonium ions or into free nitrogen.* Reduction of nitrate into nitrite and ammonia is accomplished by many micro-organisms, and is a process which has been much investigated. The biological process of nitrogen production, or of formation of oxides of nitrogen, from nitrates and nitrites, is, however, not so well understood. Nitrates form the main source of nitrogen for plant life growing in soil, and therefore ultimately for all animal life.[1] The nitrogen returns to the soil largely in organic combination, and undergoes the changes mentioned in process 2. Nitrogen is not lost to the atmosphere in its transformations in the intact plant or animal.

The total combined nitrogen on earth would increase, as a result of the biological catalytic processes of soil which fix atmospheric nitrogen, were it not for the fact that mechanisms exist which provide for the release of free nitrogen from combined forms such as nitrite or ammonia. The process whereby reduction of nitrate (or nitrite) takes place to form gaseous nitrogen (or oxides of nitrogen) is known generally as denitrification.

BIOLOGICAL NITROGEN FIXATION

It is now known that certain specific micro-organisms working symbiotically with legumes can fix atmospheric nitrogen. The following is a brief history of this discovery.

Boussingault in 1837 carried out the first quantitative field and laboratory experiments, indicating that fixation of atmospheric nitrogen takes place during the development of legumes such as clover, peas, and lucerne, whereas no such fixation occurs during the growth of such crops as wheat or oats. Liebig (1843, 1852) opposed the view that free nitrogen of the atmosphere is assimilated by the plant. He considered that the beneficial effects of the legumes are due to their large leaf surfaces, which offer greater areas for absorption of atmospheric ammonia. Ville (1855), however, showed that atmospheric ammonia is insufficient in quantity to account for the observed increase of fixed nitrogen in the development of legumes. The subject remained in a confused state until after the

[1] Ammonium nitrogen is, however, assimilated by many plants growing in soils which do not support ready nitrification, e.g. certain grasses and forest trees.

work of Lawes, Gilbert, and Pugh at the Rothamsted Experimental Station. In 1851 these investigators began experiments in an attempt to explain the results of field trials which had extended over sixteen years. The data had demonstrated that plots cropped to non-legumes without addition of manures give rise to only low yields, while plots cropped to legumes maintain high yields even without any manurial treatment. Moreover, if a non-legume follows a legume in a rotation, the yield is as high as if the field has been previously in fallow for a year. This occurs in spite of the fact that a large quantity of nitrogen is removed in the preceding leguminous crop. Liebig's explanation of absorption of atmospheric ammonia was found to be erroneous, partly because too small quantities of ammonia are absorbed from the air and partly because legumes and non-legumes behave very differently.

The logical deduction appeared to be that legume development in the field is accompanied by fixation of atmospheric nitrogen. Careful pot experiments, however, by Lawes and his colleagues (1861) gave rise to the conclusion that no fixation of molecular nitrogen takes place during the development of either legumes or cereals. The view was therefore held, and accepted for the following twenty-five years, that plants cannot fix atmospheric nitrogen. The clear-cut results of the Rothamsted field experiments still remained unexplained. The classical work of Hellriegel and Wilfarth in 1886 eventually clarified the situation. They were able to show that certain bacteria in the soil infect legumes, forming nodules which enable the plants to use atmospheric nitrogen; these bacteria have no infective power on cereals.

The organisms responsible are known as root-nodule bacteria or *Rhizobia*. They were first isolated in pure culture by Beijerinck.

NITROGEN FIXATION BY *RHIZOBIUM*

Little is known as yet of the mechanism of nitrogen fixation by the root-nodule bacteria in association with the plant. Neither the host plant nor *Rhizobium* can independently fix nitrogen, except under very specialized conditions which are under investigation. It is obvious that there must be some chemical interchange between plant and bacteria, taking place *in vivo*, which is largely responsible for nitrogen fixation. Before considering this chemical interchange, a few of the biological aspects of the association between *Rhizobia* and host plant may be mentioned.

When the seed of a legume develops in a soil containing *Rhizobia* the latter are attracted to the region of the developing root hairs. The result of the presence of the *Rhizobia* in the near neighbourhood of the root hairs is to produce a 'curling' or deformation of the hairs. Specific chemical substances are responsible for this 'curling,' for bacterial extracts in absence of *Rhizobia* are found to be as effective as the organisms themselves. The response is biologically nonspecific and may be induced by extracts of bacteria other than *Rhizobia*. At the site of deformation of the root hair, *Rhizobia* invade the root tissue and proliferate within the hair in the form of a thread directed towards the cells of the root. The migrating bacteria are embedded in a gum, and an infection thread is developed. A sheath is laid down by the host cells around the embedded bacteria. Cell division is stimulated, the newly formed tissues are invaded by more bacteria, and thus a nodule is formed. Thimann (1936) concludes that the *Rhizobia* produce in the root hair a specific compound, probably indoleacetic acid, which is responsible for the local stimulation of the host cells. Both the bacteria and the host cells fail to proliferate as the nodule becomes older, and finally the tissue becomes necrotic. The nodule softens, its interior is digested, and it finally sloughs off. The *Rhizobia* return to the soil.

There is evidence that the deformation of the root hair, essential as a preliminary to the invasion of the *Rhizobia*, is also accomplished by indoleacetic acid, a common metabolic product of bacteria. It is known that indoleacetic acid and related plant 'hormones' have but a transitory existence in soil, owing presumably to speedy decomposition by bacteria. It follows, therefore, that metabolic conditions in the soil in the near neighbourhood of the germinating legume must be such as to enable a sufficiently high concentration of indoleacetic acid to accumulate to bring about the physiological response in the root hairs. Though such a concentration may be small—of the order of one part in 100,000,000—a relatively high rate of production may be necessary to counteract the local destructive forces as work. It is known, too, that indoleacetic acid at low concentrations may be toxic to seed germination, and that tryptophane in presence of soil bacteria will induce toxicity. Thus metabolic conditions in soil will greatly influence seed germination.

The presence of combined nitrogen (e.g. nitrates or ammonium salts) in the soil in which the host plant is growing apparently makes the plant resistant to attack by *Rhizobia*. It has long been

known that nitrates impede the development of nodules on legumes: fewer root hairs are deformed and fewer nodules are formed.

Light may be thrown on the chemical association between *Rhizobia* and host plant by the recent discovery (Kubo, 1939) that haemoglobin exists as a red pigment in the nodules of legumes. Keilin and Wang (1945) have confirmed this discovery, finding that the pigment of soya-bean nodules is a haemoglobin with a characteristic absorption spectrum.

Although haemoglobin is very widely distributed in nature its presence has been considered as general only in vertebrates. This view may have to be seriously modified by the discoveries that the pigment exists in a ciliate *Paramoecium* (Sato and Tamiya, 1937) and in the root-nodules of legumes. Neither the plant cells alone nor the *Rhizobia* grown separately synthesize haemoglobin. 'It is only when root cells are invaded by a specific symbiotic micro-organism and begin to proliferate that haemoglobin is formed. *Rhizobium* not only induces growth and multiplication of cells but also supplies these proliferating cells directly or indirectly with a factor necessary for synthesis of haemoglobin' (Keilin and Wang, 1945). The facts point to the possibility that in the root-nodule haemoglobin itself, or the processes connected with its synthesis, may be directly linked with nitrogen fixation. On the other hand, haemoglobin may act only indirectly by securing in the root-nodule optimal conditions for oxidative processes with which nitrogen fixation may be associated. Carbon monoxide is known to inhibit symbiotic nitrogen fixation at low pressures, at which it reacts with haemoglobin. Virtanen and Laine (1946) have found methaemoglobin also in root-nodules, and consider that an equilibrium exists there between haemoglobin and methaemoglobin. As a result of experiments on the excretion of nitrogen products by legumes they have made an hypothesis, expressed in the following equations, relating nitrogen fixation to valency changes in haemoglobin. (They make the proviso that the hydroxylamine mentioned in the first equation need not appear directly from the molecular nitrogen but possibly only after a number of intermediate stages.)

Keilin and Smith (1947), however, deny the presence of methaemoglobin as a normal constituent of the root-nodule, and do not support the view that nitrogen fixation involves valency changes in haemoglobin.

Facts obtained by Virtanen and Laine in favour of their view are as follows:

1. Cultures of legumes in sterile sand containing the proper species of *Rhizobia* excrete *l*-aspartic acid and β-alanine, the latter probably arising from the former by decarboxylation. The excretion takes place only when nitrogen is being fixed.

2. A small quantity of oxalacetic oxime is also excreted under the same conditions.

3. Free oxalacetate is formed in pea plants actively fixing nitrogen.

4. Excised nodules, intact or crushed, are able to fix atmospheric nitrogen in presence of oxalacetate but not in its absence.

There have been failures to confirm these phenomena, but Virtanen and Laine's view offers a useful working hypothesis.

NON-SYMBIOTIC NITROGEN FIXATION

Winogradsky in 1893 found that an anaerobic soil organism, *Clostridium pastorianum*, will fix free nitrogen when supplied with glucose, the amount of nitrogen fixed being proportional to the amount of glucose broken down. The fixation of nitrogen is inhibited by the presence of ammonium salts, and this inhibition may be counteracted by an increase in the glucose concentration. Thus the ratio of carbohydrate to combined nitrogen determines the rate of fixation of nitrogen. An interesting feature of this organism is that it loses its power of nitrogen fixation during prolonged cultivation on artificial media, but the power is restored by culture of the organism once again in soil.

Beijerinck in 1901 isolated from soil and mud two aerobic organisms capable of fixing atmospheric nitrogen. They are *Azotobacter chroöcoccum* (the more common form) and *Azotobacter agilis* (the motile variety). Unlike *Clostridium*, *Azotobacter* does not lose its power of fixing nitrogen on prolonged culture on synthetic laboratory media. A striking fact concerning *Azotobacter* is that it requires for its metabolism the presence of traces of molybdenum or vanadium. A positive effect of

$$N_2 + \text{methaemoglobin (Fe}''') \rightleftharpoons NH_2OH + \text{haemoglobin (Fe}'') \quad \ldots\ldots\ldots\ldots (1)$$

$$\underset{\text{(Hydroxylamine)}}{NH_2OH} + \underset{\text{(Oxalacetic acid)}}{COOH.CO.CH_2.COOH} \rightleftharpoons \underset{\text{(Oxalacetic oxime)}}{COOH.C(NOH).CH_2.COOH} + H_2O \quad \ldots\ldots (2)$$

$$COOH.C(NOH).CH_2.COOH \xrightarrow{\text{Reduction}} \underset{\text{(Aspartic acid)}}{COOH.CH(NH_2).CH_2.COOH} \quad \ldots\ldots\ldots (3)$$

molybdenum on the growth of the organism can be observed at a concentration of 1–3 parts in 10^{12}. Burk and Horner have found that molybdenum is not only required for the assimilation of free nitrogen but is necessary for the utilization of combined nitrogen (as of asparagine or nitrate) by this organism. Tungsten will to some extent replace molybdenum. *Azotobacter* and *Clostridium* are apparently the most widely distributed non-symbiotic nitrogen-fixers in soil; they are found also in salt and fresh water, often in association with algae.

In arid soils relatively poor in organic matter, micro-organisms form more than their usual proportion (about 5 per cent.) of the organic matter, and this is chiefly due to the marked development of *Azotobacter* under the alkaline or saline conditions of such soils. In the chestnut soils of south-east Russia, where almost the whole of the organic matter is in the form of micro-organisms, there are up to 900,000,000 *Azotobacter* cells per gram of soil.

The most important single factor influencing nitrogen fixation in soils is the presence of nitrate. With both *Clostridium* and *Azotobacter* the presence of utilizable combined nitrogen diminishes the rate of nitrogen fixation, ammonium or nitrate nitrogen being effective in this way. Inhibition of fixation by *Azotobacter* is complete in the presence of ammonium nitrogen at a concentration of 0·5 mg. of nitrogen per 100 ml. The presence of nitrate or of ammonium salts in the soil also makes legumes resistant to attack by *Rhizobia*, fewer root hairs and nodules being formed. The net result is that, when excess combined nitrogen is available in the soil, little or no fixation of atmospheric nitrogen takes place. The presence of carbohydrates diminishes the effect due to the combined nitrogen.

NITROGEN FIXATION BY *AZOTOBACTER*

Kostytschew and his colleagues (1925) came to the conclusion that the initial process in fixation of nitrogen by cultures of *Azotobacter* is the formation of ammonia, and Winogradsky (1930) discovered that ammonia is formed when *Azotobacter* proliferates on a silica gel in the absence of combined nitrogen. Burk and Horner (1936) opposed the conclusion that ammonia is the first product of nitrogen fixation. They claimed that the ammonia arose in a secondary manner by oxidative deamination of cell organic matter. Winogradsky (1938) pointed out that pure cultures of *Azotobacter* cannot break down organic matter to ammonia, and concluded that the appearance of ammonia in pure cultures of this organism indicates a direct reduction of molecular nitrogen. Burk and Horner (1939), however, still maintain that the ammonia excretion of *Azotobacter* is largely independent of the form of nitrogen supplied (free or combined).

Using a manometric technique which made it possible to study nitrogen fixation by *Azotobacter* in a more quantitative manner than had hitherto been possible, Burk and his colleagues (1930, 1934) have found (1) that the respiration of *Azotobacter*, which is extremely high, is greatest at pressures of oxygen below that in air; (2) that the presence of utilizable combined nitrogen (ammonia or nitrate) diminishes the rate of free nitrogen fixation; (3) that calcium ions (or strontium ions) are necessary for the fixation, and that the substances which immobilize the calcium by forming insoluble salts with it inhibit the nitrogen fixation; and (4) that molybdenum (or, to a less extent, vanadium) has a highly beneficial effect on *Azotobacter* growth in free nitrogen.

Burk and his colleagues have suggested that the following enzyme mechanism is responsible for nitrogen fixation in *Azotobacter*:

$$N_2 + E \rightleftharpoons N_2E \text{ (rapid)},$$
$$N_2E \longrightarrow E + P \text{ (slow)}.$$

E refers to a specific enzyme (*nitrogenase*) which combines reversibly with the nitrogen molecule to form the enzyme-substrate complex N_2E. This breaks down irreversibly into *E* and the products *P*, which corresponds to an increase in *Azotobacter* cells. The total system responsible for fixation has been termed *Azotase*.

AMMONIA FORMATION

It is known that nitrogen compounds in plant residues are decomposed in soil to form ammonia so long as the ratio of carbon to nitrogen in the organic matter does not greatly exceed 10:1.

Proteins and other nitrogenous compounds are broken down in soil by a variety of organisms, the ultimate nitrogenous product being ammonia. Whether the ammonia appears or not depends on the rate of proliferation of organisms in the soil requiring the ammonia nitrogen for their own synthetic operations. If ample utilizable non-nitrogenous material, such as carbohydrate, is present, the ammonia nitrogen will not appear, as it is entirely used for building up fresh bacterial or fungal matter. The amount of nitrogen liberated as ammonia in protein decomposition may be represented as follows:

$$\left\{\begin{array}{c}\text{Nitrogen of}\\ \text{substance}\\ \text{decomposed}\end{array}\right\} - \left\{\begin{array}{c}\text{Nitrogen synthesized}\\ \text{by micro-organisms}\\ \text{for growth}\end{array} + \begin{array}{c}\text{Unassimilable}\\ \text{nitrogen}\end{array}\right\} = \left\{\begin{array}{c}\text{Ammonium}\\ \text{nitrogen}\end{array}\right\}$$

Proteins being rich in nitrogen yield ammonia in relatively large amounts. Many organisms are involved in ammonia formation, the mechanisms of which may vary from organism to organism. If the proteins are broken down to amino-acids, these may yield ammonia by the exercise of oxidase systems of either resting or proliferating micro-organisms. Little is known, however, of the modes of decomposition of nitrogenous organic matter in soil.

NITRIFICATION

The metabolic process whereby ammonia and organic nitrogenous material in soil are converted finally to nitrate was shown by Schlossing and Muntz (1877, 1874), from a study of the purification of sewage waters by land filters, to be a biological process. Warington found that soil nitrification is inhibited by application of chloroform and carbon disulphide, and both he and the Franklands (1890) established the fact that nitrification proceeds in two stages, ammonia being oxidized to nitrite and the nitrite to nitrate. Winogradsky (1890, 1891) succeeded in isolating the responsible organisms in pure culture, an achievement of great importance in the study of autotrophic organisms. Organic matter was shown to be unnecessary for the metabolism, and in fact it was stated to be injurious to their development. Warington made it clear that the final fate of nitrogen in the soil is the formation of nitrate. Progress in the study of soil nitrification since the end of last century has been extraordinarily slow. Stevens and Withers (1910) showed that nitrification in soil differs in at least one important aspect from that in the artificial (silica gel) media first elaborated by Winogradsky. They demonstrated that nitrification is inhibited far less in soil by the presence of added organic matter than in laboratory media. Much important work on the behaviour of nitrifying organisms in pure culture in laboratory media has been carried out by Meyerhof (1916, 1917) and others, but the general relations between the results obtained in such culture experiments and those obtained in soil are obscure. Albrecht and McCalla (1937) have summarized the position thus:

> The conditions controlling nitrification in aqueous solution have been studied very specifically. Less definite controls and less refinement in methods have been obtained for studies of this process within the soil. The complexity of a sand, silt, and clay mixture, as soil, prohibits an accuracy great enough to encompass all the various chemical aspects of so delicate a process as nitrification.

Lees and the present writer (1944, 1946) have carried out experiments on the mode of transformation of nitrogen compounds into nitrate in soil, using a new technique with which metabolic events in the soil can be studied with greater accuracy than has been accomplished hitherto. In essence, the attempt has been made to study a soil as though it were a living tissue. Emphasis is given to the changes brought about by the soil *as a whole* under defined experimental conditions, and care is taken that the soil itself is not interfered with throughout the experimental period. The principle is recognized that 'the biological changes taking place in soil are a direct result of the initial chemical stimulus applied to the soil, and are as much a part of the over-all chemical change as the more easily identified metabolic changes themselves' (Lees and Quastel, 1946).

An apparatus is used in the new technique whereby a column of soil (in the form of sieved air-dried crumbs) is perfused with oxygenated or aerated fluid by a circulatory process. This same soil solution is made to percolate through the soil for an indefinite period. The soil perfusate is adequately mixed and aerated and the perfusion is intermittent, so that waterlogging of the soil does not take place. The process is continuous and may be maintained for an indefinite period. The substance whose metabolism is being investigated is dissolved in the perfusion fluid or mixed with the column of soil. Analysis is confined to the constituents of the perfusate, but the soil may be examined after any arbitrary time for analysis of ions adsorbed on it. The apparatus has many advantages for the biochemical study of soil, and with it many aspects of metabolism are as amenable to study in soil as they are in plant or animal tissues. The soil is, in fact, treated as a biological whole, every effort being made to ensure constancy of the environment in which the soil is exercising its metabolic functions.

Experiments with this apparatus confirmed all earlier observations on the biological nature of soil nitrification. Further experiments gave rise to the conclusion that the rate of nitrification of a given quantity of ammonium sulphate is a

function of the degree to which the ammonium ions are adsorbed on, or combined in, the soil in the form of the soil's base-exchange complexes. The greater the amount of adsorption, the faster is the nitrification. This was shown by comparing the rates of nitrification of soils having different amounts of ammonium ions adsorbed upon them. The only tenable explanation of the results was that the adsorbed ammonium ions are those which are preferentially nitrified by the soil organisms. This led to the prediction that the addition of sterile soils to a nitrifying soil would increase its rate of nitrification in proportion to the base-exchange capacities of the added soil. This prediction was verified.

The interpretation of these results is that the nitrifying bacteria grow on the surfaces of the soil crumbs at the sites where ammonium ions are held in base-exchange combination, and proliferate at the expense of such adsorbed ammonium ions. The rate of proliferation becomes proportional, therefore, to the area of soil surface on which ammonium ions are adsorbed or combined, and is thus a function of the base-exchange capacity of the soil.

The fact that proliferation of the nitrifying organism takes place only at those specific sites of the soil surface where the ammonium ions are adsorbed leads to the conclusion that, when all these sites at the surface have been occupied, further growth of the organisms will not occur except to replace cells which have died and disintegrated. Remarkably few living nitrifying cells enter into the soil solution. This leads to the conception of a bacteria-saturated soil; that is to say, a soil where the area of proliferation is limited and cannot be extended owing to full occupancy of available sites for proliferation. Such a soil may be shown to break down substrates, specific for the organisms which enrich the soil, at constant rates. It does not exhibit the familiar logarithmic course of substrate-breakdown which obtains during proliferation. An important use may be made of such a bacteria-saturated soil. It may be made to yield information as to whether any given substance is broken down by the cells which saturate the soil. If an organic nitrogen compound, for example, is broken down and oxidized to nitrate by nitrifying cells, then the course of nitrate formation in a soil saturated with such cells should be linear, and show no initial lag period. If a lag phase does take place, the inference is that the compound in question needs attack by organisms other than the nitrifiers before nitrification can take place. In this way it has been proved that aliphatic amines, which are nitrified in soil, require organisms other than the nitrifiers to effect the initial decomposition.

An interesting new observation has been that while hydroxylamine, at small concentrations, is toxic to the nitrifying organisms and is apparently not nitrified, the presence of sodium pyruvate secures a speedy nitrification of the amine. Pyruvic oxime also undergoes rapid nitrification by a soil enriched with nitrifying organisms. In view of the hypothesis of Virtanen and Laine that oxalacetic oxime is involved in symbiotic nitrogen fixation, the fact that pyruvic oxime undergoes rapid nitrification may throw light on the mechanism whereby ammonia is oxidized to nitrate in nitrifying cells.

Another phenomenon observed by means of the perfusion apparatus is the remarkable bacteriostatic effect of potassium chlorate on the organisms that convert nitrite to nitrate. Small concentrations of chlorates (e.g. $M/10^6$) have the power of preventing the development of *Nitrobacter*, while that of *Nitrosomonas* proceeds unchecked. The result is that when nitrogenous substances are nitrified in soil in the presence of small quantities of chlorates, nitrites but not nitrates accumulate. Potassium chlorate acts as a typical bacteriostatic agent. It does not poison or interfere with the bacterial oxidation of nitrite to nitrate, for with a bacteria-enriched soil the conversion of nitrite to nitrate proceeds at a constant rate uninfluenced by concentrations of chlorate which inhibit proliferation of the organisms involved. Chlorate bacteriostasis may be neutralized by the presence of nitrates, which appear to act specifically. Explanations of these phenomena are still lacking.

LIBERATION OF FREE NITROGEN

The conditions under which this process takes place are not well understood, but it appears to be agreed that the loss of free nitrogen from the soil is greatly encouraged by poor drainage and lack of aeration. It may, however, be of considerable magnitude in well-managed cropped soils and probably also in lands still in a virgin condition.

Numerous heterotrophic organisms are known to be able to break down nitrates and nitrites with liberation of nitrogen (or oxides of nitrogen), but their quantitative significance in soils has not yet been assessed.

Nitrites react, of course, in acid or slightly acid solution with urea and amines to liberate nitrogen. It is possible, though it seems unlikely, that this chemical mechanism may form a major means by which free nitrogen leaves the soil.

Book reviews

IDENTIFICATION OF ORGANIC COMPOUNDS

Characterization of Organic Compounds, *by F. Wild. Pp.* 306. *University Press, Cambridge.* 1947. 18*s. net.*

Senior students of organic chemistry and research workers are frequently confronted with the problem of identifying organic compounds and of preparing derivatives of new substances which may serve for their future characterization. This is especially necessary in the case of liquids. Suitable derivatives should be solids with well-defined melting-points, capable of ready preparation in a state of purity. Many methods are well known, but numerous new reagents and procedures have been introduced in recent years, and if a satisfactory derivative is not readily preparable the chemist may spend much time in searching the literature.

This excellent book gives all the important general methods to the end of 1943, with full practical details for the proper preparation of the derivatives and frequently of the reagents themselves. It includes many references to original, mainly recent, papers and tables of melting-points. The arrangement of the book is according to the type of compound to be characterized. The headings include hydrocarbons, halogen and hydroxy compounds, aldehydes, ketones, acids and derivatives, and amines and various other nitrogen-containing compounds. Author and full subject indexes are provided.

The need for such a volume has long been pressing, and Dr Wild's book is destined to find an honoured place on the shelves of all organic laboratories.

W. BAKER

MATHEMATICS IN PHYSICS

Methods of Mathematical Physics, *by Harold Jeffreys and Bertha Swirles Jeffreys. Pp.* x + 679. *University Press, Cambridge.* 63*s. net.*

No one is better qualified to write a book on the methods of mathematical physics than the versatile Harold Jeffreys, now Eddington's successor at Cambridge. Here, in collaboration with Mrs. Jeffreys, herself an experienced quantum physicist, he gives a complete account of all the methods used in at least two distinct branches of theoretical physics. The reputation of the authors is in itself sufficient to recommend the book, but if anyone wants to have what is easily the most complete account of the techniques now so commonly employed he cannot possibly do better than get this volume. It is a mammoth book of nearly seven hundred pages, including as two of its chapters the well-known tracts on operational methods and Cartesian tensors, now out of print. It is not everyone's meat, but those who suddenly find themselves needing a particular technique (e.g. complex integration or the use of Fourier integrals) will get what they want here; and as they turn over the pages they will be grateful for a high standard of rigour, no loose statements, and withal a certain racy sense of humour. They will realize the quite astonishing way in which different branches of physics are unified by virtue of the mathematical methods used in discussing them. This is a volume in the best Cambridge 'big blue book' tradition.

C. A. COULSON

ANIMAL HUSBANDRY

The Breeding of Farm Animals, *by Chapman Pincher. Pp.* 149, *with* 7 *plates and* 65 *figures. Penguin Books, London.* 1946. 1*s. net.*

While plant breeding is usually done by experts, the breeding of animals is carried out by the individual farmer. This being so, it is all the more remarkable that few, if any, courses on the science of animal breeding are included in present agricultural courses at colleges and farm institutes. This book, which sets out in simple language the principles of scientific animal breeding, should therefore supply much-needed information. Chapters on genes, Mendelism, dominance, and sex linkage are well illustrated by diagrams which will greatly assist those knowing nothing of the subject.

In the introduction the author points out that in pre-war years the annual value of the edible products of British agriculture was £250,000,000, and that of this total 60 per cent. was contributed by the industry of animal husbandry. Improvements in the efficiency of animal production would therefore be to our material advantage. In a chapter on systems of breeding the uses of inbreeding, out-crossing, and grading-up are discussed, and stress is laid on the necessity for keeping records of the performance of offspring.

J. HAMMOND

AGRICULTURAL BOTANY

Principles of Agricultural Botany, *by Alexander Nelson. Pp. xviii* + 556. *Thomas Nelson & Sons Limited, London.* 1946. 35*s. net.*

The more we live in towns, the greater are our demands on the country: we all realize now that the proper use of the resources of the plant kingdom is a vital necessity. This scientific management of crop plants is a profession still in its infancy but destined for rapid expansion. For the training of recruits to this profession Dr Alexander Nelson has prepared a textbook to stand beside the *Agricultural Botany* of John Percival. In the light of his wide agricultural knowledge and his teaching experience in the University of Edinburgh, Dr Nelson puts mastery of technological details second to a grasp of principles applicable to a diversity of crops.

His first section, of 229 pages, treats of plant morphology and anatomy, furnishing among other illustrative examples five comprehensive tables for the identification of trees in winter, of common legumes, and of grasses. The second section, of 202 pages, describes the principles of plant physiology, concluding with a chapter on pasture. Section 3 introduces in 67 pages the subject of weeds, insect pests, and plant diseases. The volume concludes with a 34-page section on heredity, evolution, and classification.

Judged by wartime standards, the production has an air of refreshing opulence. There are 145 full-page plates, including 17 in colour, and 182 text figures. Almost without exception the illustrations are novel and apposite. The text is set in a well-spaced 11-point fount, and the proof-reading has been efficient.

Dr Nelson's work cannot fail to be appreciated in this country: an allocation of copies would be even more welcome overseas, where there is a pressing need for botanical textbooks with a background of British Commonwealth experience.

R. W. MARSH

IPATIEFF'S LIFE-STORY

The Life of a Chemist: Memoirs of V. N. Ipatieff, *edited by X. J. Eudin, H. D. Fisher, and H. H. Fisher, translated by V. Haensel and Mrs. R. H. Lusher. Pp. xvi + 658, with 7 plates. Stanford University Press, California; Geoffrey Cumberlege, London.* 1946. 33*s.* 6*d. net.*

Vladimir Nikolaevich Ipatieff is assured of a permanent place among the great Russian chemists. His long career, so full of variety, of light and of shade, has always borne the mark of genius. Born in 1867, Ipatieff achieved distinction in Tsarist Russia. He became Professor Ordinarius at Mikhail Artillery Academy and lecturer in the University of St Petersburg in 1902, and two years later rose to the military rank of colonel. In 1910 he was promoted to major-general, and in 1916 he was elected into the Russian Academy of Sciences. Throughout this period and for twelve years after the Revolution he cultivated with outstanding success and vigour a fruitful field of chemical research, dealing particularly with catalysis at high temperatures and pressures. As an authority on explosives and chemical warfare he became an indispensable figure in Russia during the first world war. Under the early Soviet regime he took a leading and forceful part in the development of Russian chemical industries. For all this work his country owes him a great debt. Ipatieff tells in this book the story of his life in simple and unadorned terms. He describes his scientific work only in bare outline, and fills in the background with a rich and variegated sketch of Russian life and personalities, charged with much detail of historical value. Although he held aloof from politics and tried to do his best for his country, this illustrious chemist found himself obliged in 1930 to leave for ever, as he says, 'my beloved country, my beloved Leningrad, and those laboratories in which I had spent the happiest hours of my life.' Fortunately he was able to continue his scientific work in America, as professor in the Northwestern University and Director of Research to the Universal Oil Products Company.

JOHN READ

PLASTICS FOR INDUSTRY

Plastics for Production, *by Paul I. Smith. Pp.* 216. *Chapman and Hall Limited, London.* 1946. 15*s. net.*

Today we are only too frequently told that we live in the age of plastics, and in many respects this is true. During the last ten years plastics have been playing an increasingly important part as raw materials for modern industry. Where wood or metal or ceramics had previously served we now find plastics doing the job instead.

In certain fields it is inevitable that plastics must supplant these traditional materials. But the real future of plastics lies in their use as new substances in their own right. They are taking their place alongside the established products to provide us with a more versatile and extended range of raw materials.

Unfortunately, plastics are suffering today from a surfeit of publicity, and have been attributed with almost limitless potentialities. Plastics, like other materials, have their limitations: they cannot do everything. In *Plastics for Production* we find what they can do and what they cannot. Paul I. Smith has written this book for the engineer who is looking to plastics for a raw material suitable for his work. All the common plastics are here, and their properties are discussed critically and dispassionately. For anyone in search of information that will enable him to discriminate between the multitude of plastics available to him this book should prove invaluable. J. G. COOK

DETERMINATION OF HYPER-FINE STRUCTURE

High Resolution Spectroscopy, *by S. Tolansky. Pp.* 291 + 4 *plates. Methuen and Company Limited, London.* 1947. 21*s. net.*

This is a practical account of the techniques rather than the results of high-resolution spectroscopy. A detailed consideration of the theory and performance of the Fabry-Perot and Lummer plate interferometers and of the echelon grating assumes a central position in the book, and occupies about half its length. The writing here, as elsewhere, is clear and authoritative.

A notable section of the book (and one which this reader must confess to have appreciated most) deals with light sources (67 pp.). These chapters contain first-hand, critical accounts of the experimental arrangements used for exciting spectra—the emphasis being, of course, on fine-line atomic excitation—which will prove of great interest, not only to spectroscopists in general but to workers in allied fields. Much of the information given here was previously to be found at best in scattered papers in the literature, and often only as a verbal laboratory tradition. Moreover, in times when the tendency can be discerned for research to become subordinated to apparatus-making, Dr Tolansky's descriptions of simple, elegant devices which work, and which provide answers to crucial experiments, are stimulating. A good book.

R. F. BARROW

PENICILLIN

Penicillin, its Properties, Uses and Preparations. *Pp. vi* + 199. *The Pharmaceutical Press, London.* 1946. 10*s.* 6*d. net.*

The production of penicillin is now so great that in almost all parts of the world the drug is freely available for all who need it remedially, and for research purposes. As a result large numbers of pharmacists, physicians, research workers, and others require to know the best methods of handling it. All the necessary information will be found in this excellent little book published by direction of the Council of the Pharmaceutical Society of Great Britain. Although this is essentially a practical handbook for pharmacists, the compilers have wisely recognized that the intelligent use of penicillin depends upon a general knowledge of all its properties. Consequently an account is given of the history of penicillin, its commercial manufacture, and other aspects of the subject not directly related to its pharmaceutical use. Although these less relevant aspects are necessarily dealt with quite briefly, there is an extensive bibliography for those who wish to read more widely. The sections on legislation relating to penicillin describe British and American practice, but this is similar to that followed in many other countries.

An account is given of the indications for the clinical use of penicillin and of methods of dispensing and storing solutions, ointments, creams, lozenges, and other pharmaceutical preparations containing the drug. There is also a description of the cylinder plate, serial dilution, and other standard methods of assaying penicillin.

This book can be strongly recommended, and if revised from time to time it should remain a standard work for many years.

Notes on contributors

ARTHUR HOLMES,
D.Sc., A.R.C.S., F.R.S.,

Is Regius Professor of Geology and Mineralogy in the University of Edinburgh. He was born in 1890 and was educated at Gateshead Secondary School and the Imperial College of Science and Technology, London. His first research—on the accumulation of lead in radioactive minerals, carried out under the guidance of Lord Rayleigh—was interrupted by a period of geological exploration in Mozambique, after which he returned to Imperial College as a Demonstrator in Geology (1912). In 1920 he went to Burma as chief geologist of the Yomah Oil Company. In 1924 he was appointed Reader of Geology, and three years later Professor, in the Durham Division of the University of Durham, which post he continued to hold until 1933. He served as Exchange-Professor at Basle in 1931, and as Lowell Lecturer at Boston in 1932. His chief scientific interests are problems of petrology and petrogenesis, and the applications of radioactivity to geology. Besides having made many important contributions on these subjects to scientific journals, he is the author of several well-known books. He has been an active member of the National Research Council Committee on the Measurement of Geologic Time since its foundation. In 1940 he was awarded the Murchison Medal of the Geological Society of London.

MURRAY MACGREGOR,
M.A., D.Sc., F.R.S.E., F.G.S.,

Is a graduate of Glasgow University. He joined the Geological Survey in 1909, became a district geologist in 1919, and in 1924 was appointed Assistant Director in charge of survey activities in Scotland. This post he held until his retirement in 1945. In the course of his career he has made many contributions to official publications and to scientific periodicals, mainly in the sphere of stratigraphical, economic, and glacial geology. He achieved conspicuous success in organizing increasingly detailed work on Scottish mineral deposits and in promoting close collaboration with the mining and industrial community. His services to geology have been recognized by the award of the Murchison Medal of the Geological Society of London in 1941, and of the Clough Memorial Medal for Geology of the Edinburgh Geological Society (1942–4). Dr Macgregor is a past president of the Geological Societies of Glasgow and of Edinburgh, a past vice-president of the Geological Society of London, and editor of the *Transactions of the Glasgow Geological Society*. He is at present president of the Geological Section of the British Association for the Advancement of Science.

L. M. ANGUS-BUTTERWORTH,
M.A., M.I.Mech.E., F.R.G.S.,
F.S.A. (Scot.),

Was educated at the Department of Glass Technology, University of Sheffield, and at the Universities of Manchester and Toulouse. He is a director of the Newton Glass Works, Manchester, founded in 1795. A Fellow of the Society of Glass Technology, he is at present chairman of the North-East Section. He has written a book, *The Manufacture of Glass*, to be published this year by Sir Isaac Pitman & Sons Limited. He is a past chairman of the Manchester Literary and Philosophical Society and *Membre Honoraire de l'Institut Historique de France*. He is also a governor of the Royal Scottish Corporation and the Royal Caledonian Schools.

D. STARKIE,
M.Sc., Ph.D.,

Was born in 1904 and was educated at Netherthorpe Grammar School, Staveley, and the University of Sheffield, where, after graduating, he served for some time on the teaching staff. He then took charge of the Optics and Illuminating Laboratories of the Metropolitan-Vickers Electrical Company at Manchester, and later became chief physicist at the Wear Glass Works (Sunderland) of J. A. Jobling and Company. Upon his appointment as head of the Physical Section of the Plastics Division's Research Department of Imperial Chemical Industries, he initiated investigations on optical plastics. The research developed along original lines and by 1945 had become so promising that a separate optical department was established with Dr Starkie in charge. Dr Starkie is well known throughout the optical industry in Britain, and is a member of the council of the British Scientific Instrument Research Association.

M. SCHOFIELD,
M.A. (Oxon.), D.Sc. (Lond.), F.R.I.C.,

Was educated at Bradford Grammar School and at Magdalen College, Oxford, where he was an Open Scholar in Natural Science from 1920 to 1924. After leaving Oxford he became senior science master at Worksop College, and is now Responsible Lecturer in Chemistry at Wolverhampton and Staffordshire Technical College. He is author of a considerable number of studies, both on biographical subjects and chemical history, published in *Chemistry and Industry*, *Discovery*, *Science Progress*, etc. He has also contributed reviews of industrial progress to supplements of *The Times* and to various journals of chemical industry and technology. For some years he studied the wood distillation industry, and published original papers on the subject in the *Transactions of the Institute of Chemical Engineers* and other technological journals.

J. H. QUASTEL,
M.A., D.Sc., Ph.D., F.R.I.C., F.R.S.,

Was director of the Soil Metabolism Unit at University College, Cardiff, until this year, but has now been appointed Professor of Biochemistry at McGill University and Associate Director of the Institute of Cell Metabolism, Montreal. He was born in 1899 and was educated at the Central Secondary School, Sheffield, the Imperial College of Science, London, and Trinity College, Cambridge. He served in the war of 1914–18 and on demobilization studied chemistry at the Royal College of Science, London, afterwards carrying out research in the School of Biochemistry, Cambridge (1921–9). His work there was mainly devoted to the biochemistry of bacteria. In 1929 he was appointed Director of Research at Cardiff City Mental Hospital and carried out researches on the biochemistry of the central nervous system and the mechanism of the action of narcotics and benzedrine. He was the first to show the synthesis of acetylcholine in isolated brain tissue and to study fat metabolism in isolated surviving tissue slices. He has worked on enzyme systems in brain and other tissues and has correlated clinical with laboratory results in the investigation of mental disorder and treatment. In 1941 he was appointed director of the Agricultural Research Council Unit of Soil Biochemistry.

Made and printed in Great Britain at THE KYNOCH PRESS, *Witton, Birmingham, 6, for the publishers,*
IMPERIAL CHEMICAL INDUSTRIES LIMITED, *London*, S.W.1